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FLAME AND COMBUSTION IN GASES

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"*The power of Fire, or Flame, for instance, which we designate by some trivial chemical name, thereby hiding from ourselves the essential character of wonder that dwells in it as in all things, is with these old Northmen, Loke, a most swift subtle* Demon *of the brood of the Jötuns. . . . From us too no Chemistry, if it had not Stupidity to help it, would hide that Flame is a wonder. What* is *Flame?*"

(CARLYLE on "Heroes"—Odin and Scandinavian Mythology.)

FLAME
AND
COMBUSTION
IN GASES

BY

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M.A., D.Sc., F.R.S.

AS THE FOUNDER AND DOYEN OF
THE MANCHESTER SCHOOL OF
COMBUSTION RESEARCH

Explosions, Explosions in Closed Vessels, the Mechanism of Gaseous Combustion, and Catalytic Combustion, respectively, in the order named. At the end of each section is appended a bibliography of the principal researches discussed in it. Also, by the kind permission of the International Research Council, we have been able to reproduce in an Appendix the collected numerical data on Gaseous Explosions which we contributed to the International Critical Tables.

It has not been an easy matter to select from the huge literature of the past fifty years the particular researches which have contributed most to the general progress, nor yet to preserve proper balance between the various parts of the subject, because of the unconscious bias of an investigator to exaggerate the importance of those parts of it in which he himself is more particularly interested. We do not pretend to have escaped this tendency, for we have dealt chiefly with those aspects of the subject about which we know most at first-hand.

Naturally we have dealt with the chemical aspects of the subject; physicists and engineers may find much to criticise and regard as inadequate. We have avoided entering into discussions of the special problems of the internal combustion engine, because they have been so fully dealt with in Sir Dugald Clerk's treatise on the subject, and it would have been an impertinence on our part to trespass on the territory which he has made so peculiarly his own. There are also many other practical aspects of the subject—such as those relating to the industrial uses of gaseous fuel, the design of burners, and the question of safety in mines and factories—which doubtless might have been dealt with, but we have limited ourselves to an exposition of the underlying principles of gaseous combustion as disclosed by modern researches.

We are deeply indebted to many of our friends and colleagues for their help and encouragement in our task. Especially would we thank in this connection Professors H. E. Armstrong, H. B. Baker, J. B. Cohen, W. T. David, H. B. Dixon, A. Fowler, A. Smithells, W. M. Thornton, and R. V. Wheeler, as well as Sir Dugald Clerk and Mr. H. T. Tizard, all of whom have freely permitted us to make the fullest use of their publications and to reproduce from them such illustrations as we might desire.

As some of the recent researches described in Chapters XII., XIII., XIV., XXVI. and XXVII. have been the outcome of the Gas Research Fellowships established at the Imperial College, London, by The Gas Light and Coke Company and Radiation Limited, our thanks are due to Sir David Milne-Watson and Mr. H. James Yates for their generous support of them; to Mr. Yates we are also indebted for permission to reproduce in Chapter XVII. an infra-red spectrogram from a Bunsen flame taken in the Radiation Research Laboratories. We also owe much to the interest which Mr. Robert Mond has shewn in these researches.

We would also express our indebtedness to the Councils of the Royal Society and the Chemical Society for permission to use diagrams, etc., from their publications, and especially to the Council of the Royal Society for permission to reproduce in Chapters XII., XIII. and XIV. (with slight alterations), papers recently contributed to their *Proceedings* from our Research Laboratories at the Imperial College of Science and Technology, London, as well as to the International Research Council for a similar favour in respect of an Appendix, as aforesaid. We also desire to thank the proprietors of the *Philosophical Magazine*, the Controller of H.M. Stationery Office, as well as the Councils of the Institution of Mining Engineers and the Institution of Gas Engineers for permission to reproduce illustrations from their publications. We are also under similar obligations to numerous other authors and investigators, whose researches we have referred to, and we trust that they will accept this general acknowledgement.

We desire especially to thank our colleague, Mr. W. E. Stockings, M.Sc., for his unstinted and most valuable help in reading through the proofs, as well as for many suggestions in regard to the text, also Captain G. I. Finch and Dr. D. M. Newitt of the Imperial College of Science and Technology, London, for help in connection with particular chapters.

WILLIAM A. BONE.
DONALD T. A. TOWNEND.

THE IMPERIAL COLLEGE OF SCIENCE
AND TECHNOLOGY,
LONDON, 30*th April*, 1927.

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SECTION I

CHAPTERS I TO VII

HISTORICAL REVIEW

PARTICULARLY OF THE PERIOD 1660-1880

CHAPTER I

THE RESEARCHES OF AN OXFORD SCHOOL OF CHEMISTS
1660 TO 1679

ROBERT BOYLE, ROBERT HOOKE, AND JOHN MAYOW

THE experimental study of combustion may be said to have commenced with the Oxford School of Chemistry under the leadership of Robert Boyle about the time of the Restoration. In the previous year, with the assistance of his pupil Robert Hooke, Boyle had contrived his 'Machina Boyleana,' a forerunner of the modern air-pump, and soon afterwards proved by experiment that neither charcoal nor sulphur burns when strongly heated in vessels exhausted of air, although each inflames as soon as it is re-admitted. Also, a mixture of either substance with nitre was found to catch fire even when heated in a vacuum. These experiments, revealing as they did the dependence of combustion upon the action of something common to both air and nitre, led Boyle to conclude: "For though by reason of its great thinness and of being in its usual state devoid both of taste and smell, air seems wholly unfit to be a menstruum (*i.e.* solvent), yet it may have a dissolving or at least a consuming power on many bodies, especially such as are peculiarly disposed to admit its operations. . . ." * He suspected "that there may be dispersed thro' the atmosphere, some odd substance . . . on account whereof, the air is so necessary to the subsistence of flame." He thought that in the calcination of metals a ponderable 'fire-stuff' is taken up, thus accounting for the gain in weight which Jean Rey had observed in 1630.

In 1665 Robert Hooke, in his *Micrographia* argued against the ancient doctrine that 'fire' is an element, and gave, in the following series of propositions, a new view of combustion, as well as a beautiful definition of flame, which came near to our modern ideas. He wrote:

"First, that the Air in which we live, move, and breath, and which encompasses very many, and cherishes most bodies it encompasses, that this Air is the menstruum, or universal dissolvent of all Sulphureous bodies.

---

* *Suspicions about some Hidden Qualities of the Air*, p. 77.

"Secondly, that this action it performs not, till the body be first sufficiently heated, as we find requisite also to the dissolution of many other bodies by several other menstruums.

"Thirdly, that this action of dissolution produces or generates a very great heat, and that which we call Fire; and this is common also to many dissolutions of other bodies, made by menstruums, of which I could give multitudes of Instances.

"Fourthly, that this action is perform'd with so great a violence, and does so minutely act, and rapidly agitate the smallest parts of the combustible matter, that it produces in the diaphanous medium of the Air, the action or pulse of light, which what it is, I have else-where already shewn.

"Fifthly, that the dissolution of sulphureous bodies is made by a substance inherent, and mixt with the Air, that is like, if not the very same, with that which is fixt in Saltpeter, which by multitudes of Experiments that may be made with Saltpeter, will, I think, most evidently be demonstrated.

"Sixthly, that in this dissolution of bodies by the Air, a certain part is united and mixt, or dissolv'd and turn'd into the Air, and made to fly up and down with it in the same manner as a metalline or other body dissolv'd into any menstruums, does follow the motions and progresses of that menstruum till it be precipitated.

"Seventhly, that as there is one part that is dissoluble by the Air, so are there other parts with which the parts of the Air mixing and uniting, do make a Coagulum, or precipitation, as one may call it, which causes it to be separated from the Air, but this precipitate is so light, and in so small and rarify'd or porous clusters, that it is very volatil, and is easily carry'd up by the motion of the Air, though afterwards, when the heat and agitation that kept it rarify'd ceases, it easily condenses, and commixt with other indissoluble parts, it sticks and adheres to the next bodies it meets withall: and this is a certain Salt that may be extracted out of Soot.

"Eighthly, that many indissoluble parts being very apt and prompt to be rarify'd, and so, whilst they continue in that heat and agitation, are lighter than the Ambient Air, are thereby thrust and carry'd upwards with great violence, and by that means carry along with them, not onely that Saline concrete I mention'd before, but many terrestrial, or indissoluble and irrarefiable parts, nay, many parts also which are dissoluble, but are not suffer'd to stay long enough in a sufficient heat to make them prompt and apt for that action. And therefore we find in Soot, not onely a part, that being continued longer in a competent heat, will be dissolv'd by the Air, or take fire and burn: but a part also which is fixt, terrestrial, and irrarefiable.

"Ninthly, that as there are these several parts that will rarifie and fly, or be driven up by the heat, so are there many others, that as they are indissoluble by the aërial menstruum, so are they of such sluggish and gross parts, that they are not easily rarify'd by heat, and therefore cannot be rais'd by it; the volatility or fixtness of a body seeming to consist only in this, that the one is of a texture, or has component parts that will be easily rarify'd into the form of Air, and the other, that it has such as will not, without much ado, be brought to such a constitution; and this is that part which remains behind in a white body call'd Ashes, which contains a substance, or Salt, which Chymists call Alkali: what the particular natures of each of these bodies are, I shall not here examine, intending it in another place, but shall rather add that this Hypothesis does so exactly agree with all Phoenomena of Fire, and so genuinely explicate each particular circumstance that I have hitherto observ'd, that it is more then probable, that this cause which I have assign'd is the true adequate, real, and onely cause of those Phoenomena; and therefore I shall proceed a little further, to shew the nature and use of the Air.

"Tenthly, therefore the dissolving parts of the Air are but few, that is it seems of the nature of those Saline menstruums, or spirits, that have very much flegme mixt with the spirits, and therefore a small parcel of it is quickly glutted, and will dissolve no more; and therefore unless some fresh part of this menstruum be apply'd to the body to be dissolved, the action ceases, and the body leaves to be dissolv'd and to shine, which is the Indication of it, though plac'd or kept in the greatest heat: whereas Saltpeter is a menstruum, when melted and red-hot, that abounds more with those Dissolvent particles, and therefore as a small quantity of it will dissolve a great sulphureous body, so will the dissolution be very quick and violent.

"Therefore in the Eleventh place, it is observable, that, as in other solutions, if a copious and quick supply of fresh menstruum, though but weak, be poured on, or applied to the dissoluble body, it quickly consumes it: So this menstruum of the Air, if by Bellows, or any other such contrivance, it be copiously apply'd to the shining body, is found to dissolve it as soon, and as violently as the more strong menstruum of melted Nitre.

"Therefore twelfthly, *it seems reasonable to think that there is no such thing as an Element of Fire* that should attract or draw up the flame, or towards which the flame should endeavour to ascend out of a desire or appetite of uniting with that as its Homegeneal primitive and generating Element: *but that that shining transient body which we call Flame, is nothing else but a mixture of Air, and volatil sulphureous parts of dissoluble or combustible bodies, which are acting upon each other whil'st they ascend*, that is, flame seems to be a mixture of Air, and the combustible volatil parts of any body, which parts the encompassing Air does dissolve or work upon, which action, as it does intend the heat of the aërial parts of the dissolvent, so does it hereby further rarifie those parts that are acting, or that are very near them, whereby they growing much lighter than the heavie parts of that Menstruum that are more remote, are thereby protruded and driven upwards : and this may be easily observ'd also in dissolutions made by any other menstruum, especially such as either create heat or bubbles. *Now, this action of the Menstruum, or Air, on the dissoluble parts, is made with such violence, or is such, that it imparts such a motion or pulse to the diaphanous parts of the air, as I have elsewhere shewn is requisite to produce light.*"

In 1674 John Mayow, another of Boyle's pupils and an experimentalist of the first rank, described in his *Tractatus Quinque Medico-Physici* a remarkable series of experiments upon combustion from which he developed a theory which, whilst in certain aspects outwardly resembling the one propounded by Lavoisier a century later, yet in others undoubtedly differed from it.* His ideas, although tinged with alchemical notions, shewed great penetration of mind and were much in advance of his day.

In common with Hooke, Mayow regarded heat and light as originating in the motions of particles. These, he thought, may be of three kinds, namely (1) the 'nitro-aërial' particles, which may be linked to the particles of air and also are present in nitre, (2) the 'sulphureous' or inflammable particles, which are contained in all combustible substances, and (3) 'saline' particles, which may be fixed or volatile. Thus he said :

"Among the principles of natural things the nitro-aërial spirit holds the chief place, which is deservedly called mercury, inasmuch as it is a highly subtle, mobile, and ethereal substance, and is the primary instrument of life and motion, not only in plants, but also in animals. Among the principles of the peripatetics the two chief ones are fire and air, by both of which our nitro-aërial mercury may be rightly substituted, inasmuch as it possesses a truly igneous nature, and, moreover, constitutes a highly active and fermentative part of the air." The nitro-aërial spirit produces very different effects, whether it is at rest or in motion.

"Sulphur lays claim to the next place, and this principle, after the nitro-aërial mercury, is the most fermentative, and thus only these two principles seem to be active. The condition of sulphur seems to alter, for at one time it is inert and asleep, and at another it is roused into activity, and again it becomes turbulent and savage.

"The nitro-aërial spirit and sulphur exercise a perpetual hostility, and in the mutual conflict brought about by their meeting, according as the one or the other prevails, changes seem to arise.

---

* This view of the matter was convincingly put forward by Prof. Julius B. Cohen, F.R.S., in an Address upon Mayow's work, entitled "A Student of the Early English School of Chemistry," delivered to the Yorkshire College Chemical Society on the 24th October, 1901, and subsequently printed in separate form. It was this address which first directed our attention to the peculiar features of Mayow's theory which so clearly differentiates it from that of Lavoisier, and we also make use of Prof. Cohen's translation of the *Tractatus.*

"In the third place, salt must be added to the principles, and this contains the passive property ; for however salt may be volatilised, I do not think the internal motion originates with it. The salt is fixed or volatile ; nevertheless, both are of the same nature ; but the state of the salt is more altered when it is changed from pure salt into acid.

"A great affinity and kinship exists between salt and nitro-aërial spirits, as also between it (salt) and sulphur, for these highly active principles are attached in turns to the salt as if they were wedded to a proper spouse.

"Besides the above principles there is also to be found in nearly everything, both water and earth (terra damnata). Water seems to be the suitable vehicle for the nitro-aërial spirit and sulphur, and it, together with the earth, assists in building up the structure of things with proper consistency and mass."

Mayow had reached the conclusion that, although nitre *as such* does not float about invisibly in the air, else would the flame of a lamp crackle, yet a certain nitrous and acid spirit seems to reside in the air, and is necessary for combustion. "I think," he said, "that it must be conceded that something aërial, whatever it may be, is necessary for kindling any flame. The experiments of Boyle have placed this beyond a doubt, from which it follows that a lighted lamp will expire more quickly in an evacuated receiver than in the same filled with air, which is manifest proof that the flame enclosed in the receiver is extinguished not so much by its own smoke, as some thought, as by being deprived of its aërial sustinance. . . ."

By making the now familiar experiment of burning a candle in a bell-jar of air enclosed over water, Mayow had observed that air is diminished in bulk by combustion, and that when the flame expires the residual air is inactive and will not support combustion. Also, he had found that the respiration of animals in an enclosed air-space has the same effect, and therefore concluded that respiration and combustion are analogous processes. He also knew that in many cases combustion produces acidic substances. He thus describes his experiment :

"A burning candle is so disposed in water that the burning wick projects about six fingers' breadth above the water, then a tall inverted glass vessel is placed over the light. But care must be taken that the surface of the water enclosed in the glass equalises the height of the water outside." He effected this by means of a little syphon. "These being prepared, the vessel is firmly held, lest it may descend further into the water, and when the light hath burnt to a certain point you will perceive the water slowly rising in the vessel." * He repeated this experiment with other inflammable materials.

"I am accustomed to suspend a bit of camphor to which tinder dipped in a little sulphur is affixed." The vessel was then inverted over water, the pressure equalised as before, and the sulphur ignited by means of a burning glass. "Which being done, you perceive the water within, by reason of the motion of the igneous particles and rarefaction of the air within, to descend, but after the light hath gone out, the air enclosed in the vessel at once cools, and returns to its original state, and thus the water inside is found to have risen above one-half of that at first noticed, and by calculations it is found that the air is reduced by about a thirtieth less than before. After the fumes of the light by which the vessel is filled hath passed away. . . . I have tried to kindle it a second time by projecting as before the sun's rays on a second piece of camphor suspended in the glass vessel; but the experiment did not succeed." *

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* *Tractatus*, chap. vii. p. 98.

He then put forward his explanation of the facts so observed, as follows: The candle flame in time went out because the air enclosed in the vessel was deprived of its nitro-aërial particles by the combustion so that it ceased to be capable of maintaining the flame; the nitro-aërial particles are normally linked to the aërial particles as if by little hooks, and so give elasticity to them; on burning, the nitro-aërial particles are drawn out from the air and destroyed ("atque eas per flammae de flagrationem ab aere exhauriri et absumi"), so that the elasticity of the aërial particles is diminished and they contract.

As to the origin of the nitro-aërial particles, Mayow supposed that the sun is a vast reservoir of them, from whence they pass to the upper regions of the earth's atmosphere. Here they meet with, and become linked to, aërial particles, which are thereby renovated, and afterwards sink down to the earth's surface to promote combustion and respiration. In such wise, the aërial particles, being constantly exhausted and reduced in weight by combustion and respiration at the earth's surface, fly to the upper regions of the atmosphere, where they are renovated by linking up with the nitro-aërial particles, which originate in the sun; and it is only by this constant renovation of the otherwise inert aërial particles that life on earth can be maintained. "If it were not for this," said Mayow, "there might be no society of men, nor yet indeed of animals."

The essential features of Mayow's theory may be summarised as follows: Two things are requisite for combustion, namely (*a*) the sulphureous or inflammable particles which exist in all combustible substances, and (*b*) nitro-aërial particles which, originating in the sun, become linked to the aërial particles (which *per se* are inert) in the upper atmosphere, whereby the air is constantly renovated and made capable of supporting combustion and life. The two kinds of particles (*a*) and (*b*) are mutually so hostile that when suitably brought together they enter into sharp conflict, whereby they are thrown into violent motions, resulting in the appearance of fire. And it is clear that such a view, although far advanced for its day, differs from that propounded by Lavoisier a century later in that (i) it did not recognise that common air is a mixture of two physically similar but chemically distinct gases, the one *active* and the other *inert* in combustion, and (ii) that it regarded combustion only as the interplay, and not the actual combining, of two opposite kinds of particles.

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* *Tractatus*, chap. vii. p. 101.

It would appear that, so far as his general views are concerned, Mayow followed very much those of his contemporaries, *i.e.* in assuming matter to be composed of such principles as salt, sulphur and mercury, together with water and earth. In place of mercury, however, he substituted his hypothetical nitro-aërial particles. One experiment of his, namely the oxidation of antimony placed on a marble slab in contact with air under the influence of the sun's rays focussed upon the metal, has sometimes been referred to as proving that Mayow had anticipated Lavoisier's discovery that the increase in weight was due to the fixation by the metal of one particular constituent (oxygen) of the air. Mayow, however, attributed it to the fixation of nitro-aërial particles, which were assumed to have come from the sun, concentrated on the metal by means of the lens. Thus to quote his own description: "I am not ignorant of the common opinion that the diaphoretic value of antimony is attributed to its combustible sulphur being consumed in calcination, but I doubt if it is consistent with the truth. . . . It is probable that it is the nitro-aërial particles with which the spirit of nitre is filled and in some motion of which the sun's rays consist, which fix the antimony and render it diaphoretic. . . . And the facts point to this conclusion, that antimony acquires its diaphoretic virtue not only from spirit of nitre and from the sun's rays, but also from the flame of nitre in which nitro-aërial particles are more densely packed. Nor must we overlook the fact that antimony calcined by the sun's rays increases considerably in weight, as is shown by experiment, and it is impossible to conceive whence that weight of antimony proceeds unless from the nitro-aërial particles fixed during calcination." Indeed, in spite of the excellence of his experiments, and the ingenuity of his interpretation of them, from a modern standpoint, his theory seems fantastic.

It may be that, but for his death in 1679 at the age of thirty-six, Mayow would have carried his experiments further and discovered the gas now called oxygen; but, although he may have been on the verge of such a discovery, he did not actually make it. As Professor Cohen (*loc. cit.*) justly says, "he was a light shining in the darkness; but shining in vain, for there was none, either among his contemporaries or his successors, to reflect his teachings."

CHAPTER II

THE RISE AND FALL OF THE PHLOGISTON THEORY AND THE ERA OF PNEUMATIC CHEMISTRY

1680 TO 1800

STAHL, BLACK, CAVENDISH, SCHEELE, PRIESTLEY AND LAVOISIER

The Phlogiston Theory

Soon after Mayow's death in 1679 another view of combustion, known as the Phlogiston Theory, began to gain ground. It originated with J. J. Becher (1635 to 1681), who attempted to revive in another form some of the ideas of Basil Valentine and Paracelsus concerning the constitution of things; in 1702 it was considerably developed by G. E. Stahl (1660 to 1734), and soon became universally accepted amongst chemists to the complete obscuration of the teachings of Boyle, Hooke and Mayow.

According to the phlogistonists, all combustible bodies contain at least two 'principles,' one of 'combustibility,' called phlogiston,* which escapes during combustion, and the other of 'incombustibility,' which remains behind. Thus a metal was supposed to be compounded of phlogiston and an earthy residue (the calx), so that on its being calcined the former escapes and the latter remains. More easily combustible substances, such as coal, charcoal, sulphur or phosphorus were supposed to consist so largely of phlogiston that after its escape during combustion little or no visible residue remains.

The theory was really a throw-back to the old alchemistic notion that the qualities of things are due to the presence in them of a few subtle 'principles' whose ebb and flow cause natural phenomena. The principle resident in all combustible bodies was supposed by Stahl to be one and the same phlogiston; and, that on escaping from them sufficiently rapidly during combustion, it assumes a violent whirling motion causing the appearance of fire. He supposed that this phlogiston can be transferred from one substance to another.

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* This was the word coined for it by Stahl; Becher had called it '*terra pinguis*'; but the idea of a subtle principle common to all combustible substances dates back to alchemistic times.

It was of course known to the phlogistonists that metals increase in weight on calcination ; but instead of this fact being regarded as subversive of their theory, it only led them to ascribe to 'phlogiston' a *negative* weight, so little had the Newtonian conception of things influenced contemporary chemical thought, which still remained essentially alchemical, in that the *form* of bodies rather than their *mass* was considered to be their most essential property.

The phlogiston theory dominated chemistry during the greater part of the eighteenth century ; but its foundations were shaken by the experiments of Joseph Black upon magnesia alba, quicklime, and other alkaline substances in 1754, and it did not long survive the discovery of oxygen by Scheele and Priestley twenty years later. It won the full assent of such distinguished chemists as Cavendish, Marggraf and Scheele, all of whom constantly explained their researches in terms of it ; whilst Priestley passionately defended it until his death in 1804. The 'inflammable air' (hydrogen) given off when certain metals are dissolved in dilute acids was thought to be identical with 'phlogiston' by several chemists, including at one time Cavendish, although after his discovery in 1781 that water is the only product of its combustion, he regarded it as a compound of phlogiston and water.

Erroneous though it was, the doctrine of phlogiston rendered a great service to science in that it led men clearly to recognise for the first time that what are now called the processes of 'oxidation' and 'reduction' are really opposites and reversible, and it undoubtedly stimulated enquiry and research. Stahl also recognised the analogy between respiration and combustion, and assigned the chief rôle in each to 'phlogiston.' The value of the theory was that it enabled a variety of similar processes to be interpreted from a common point of view. Indeed it has sometimes been said that if the word 'energy' were substituted for 'phlogiston' in its tenets, the theory would still hold ; but surely this puts too great a strain upon the implication of the two words.

After its final overthrow by Lavoisier the theory ceased to have more than an historical interest for chemists, and passed completely out of laboratories into books and libraries.

The Era of Pneumatic Chemistry (1750–1800)

THE WORK OF BLACK, CAVENDISH, SCHEELE, PRIESTLEY AND LAVOISIER

The most powerful weapon for the overthrow of the phlogiston theory was forged by the experimental researches of Black, Cavendish, Scheele, and Priestley in the field of pneumatic chemistry during the period 1766 to 1781. Up to that time the term 'air' had been associated with the idea of an invisible and elementary elastic fluid upon which special qualities might be imposed without any real change in its fundamental character. According to this idea, varieties of 'air' were possible, such for instance as the 'inflammable air' (hydrogen) discovered by Paracelsus, or the 'gas sylvestre' (carbon dioxide) described by Van Helmont, but these were considered as due to the imposition of some special quality upon 'air.' Indeed, very little was known about gases from a chemical point of view, and neither Boyle nor his contemporaries could say whether or not either 'inflammable air' or 'gas sylvestre' differed materially from atmospheric air; and the notion that all gases were merely 'air' with various 'admixtures' prevailed right up to the middle of the eighteenth century.

Black may be said to have originated the idea of chemically distinct species of gases by shewing, in 1755, that there is a 'particular species' of air, which he termed '*fixed air*,' dispersed in small quantity through the atmosphere, and differing from ordinary air in that it can be absorbed and 'fixed' by caustic alkalies, whereby their causticity is lost, and that the same gas is again liberated unchanged when a mild alkali (such as limestone or magnesia alba) is either calcined or dissolved in acids. Also, Cavendish, who in 1766 investigated 'inflammable air' (hydrogen) pronouncing it to be 'phlogiston,' did much to clear away the old misconception.

It was, however, the discovery of several new gases by Joseph Priestley and Carl Wilhelm Scheele during the years 1767 to 1777 which finally clarified the whole position and laid the foundation of our modern gas chemistry. These two great experimentalists worked independently, and at the time unknown to each other, and it is remarkable how their discoveries overlapped. Priestley, whose work on gases began at Leeds soon after the year 1767, published his discoveries in a series of five volumes entitled *Experiments and Observations on Different Kinds of Air* between the years 1774 and 1780; those of Scheele are chiefly to be found in his celebrated *Chemical Treatise on Air and Fire*, published in 1777.

Joseph Priestley (1733 to 1804)—a dissenting minister and philosopher, renowned for his theological works and discoveries in pneumatic chemistry—was one of the most remarkable personalities of the age in which he lived. His liberal views, which he fearlessly advocated, raised such bitter and violent opposition in his own country, culminating in the celebrated Priestley riots in Birmingham (1794),—when the mob burnt his house, books, manuscripts and instruments—that eventually, in 1794, he had to remove to America, where he was well received, and where he died in 1804.

Of his scientific work Thomas Huxley finely said * that "without the careful scientific training of Black, without the leisure and appliances secured by the wealth of Cavendish, he scaled the walls of Science as so many Englishmen have done before and since his day; and trusting to mother wit to supply the place of training, and to ingenuity to create apparatus out of washing tubs, he discovered more new gases than all his predecessors put together had done."

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* *Science and Culture*, p. 107.

He designed, and was the first to use, the pneumatic trough, and may be said to have laid the foundations of gas-analysis. Commencing with experiments upon fermentation at a brewery near his house in Leeds in 1767, he used 'fixed air' (carbonic acid gas) to aërate water, so conferring on thirsty mankind the boon of soda-water. Soon afterwards (1772) he found that air is vitiated ('phlogisticated'), by both the combustion of candles and the respiration of animals, and that on exposing such deteriorated air to the action of living plants in sunlight its former qualities are restored. He discovered nitrous oxide ('dephlogisticated nitrous air'), first characterised nitric oxide ('nitrous air'), and discovered oxygen. He was the first to isolate many gases—*e.g.* ammonia ('alkaline air'), hydrogen chloride ('marine acid air'), sulphurous acid ('vitriolic acid air'), and silicon tetra fluoride ('fluor acid air')—by collecting them over mercury. Also, he observed the formation of water when a mixture of inflammable air (hydrogen) and atmospheric air is exploded in a copper vessel. Notwithstanding that his discoveries provided Lavoisier with weapons to over-throw the phlogiston theory, Priestley was unable to see their real significance and remained to the end an ardent and uncompromising supporter of it.

Carl William Scheele (1742–86) was an obscure Swedish apothecary, living a solitary life, hampered by poverty and harassed by debt—yet, as Sir Edward Thorpe wrote of him, "he succeeded by the sheer force of his genius as an experimentalist, and under the influence of a passion which defied difficulty and triumphed over despair, in changing the entire aspect of a science." * He served chemistry with a pure and noble devotion ('*Diese edel Wissenschaft est meine Auge*'), following her with patience and humility, and enriching her with a wealth of new discoveries. Among these were chlorine ('dephlogisticated muriatic acid'), oxygen ('fire air'), prussic acid, glycerine and a whole series of organic acids, including oxalic, tartaric, citric, malic, gallic, uric, lactic and mucic acids; indeed he may be said to have founded organic chemistry.

The crowning achievement of these two men was the discovery of the gas which we now call oxygen, and it came about as follows:

In or about the year 1773, Scheele, who was a convinced phlogistonist and always worked according to some definite and logical plan, had burned such substances as phosphorus, 'inflammable air' or a candle in a confined volume of air, in each case for so long as the flame would continue. And he always found that between one-third and one-fourth of the original air had disappeared. From this circumstance he concluded "that the air consists of two fluids, differing from each other, the one of which does not manifest in the least the property of attracting phlogiston, while the other, which composes between the third and the fourth part of the whole mass of the air, is peculiarly disposed to such attraction. But where this latter kind of air has gone to after it has united with the inflammable substances is a question which must be decided by further experiments, and not by conjectures." He was, however, not able to find the lost air again, for he was satisfied that it did not remain in the 'residual air,' which could no more unite with phlogiston, and was actually lighter than ordinary air.*

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* *Essays in Historical Chemistry*, p. 53.

He was thus led to suppose that, inasmuch as presumably phlogiston had been given off from the combustible body, and as actually some part of the air had disappeared during the experiment, they might have combined and escaped in the form of heat, which undoubtedly had passed through the walls of the containing vessel. If so, he argued, heat must be compounded of phlogiston and that part of common air which had disappeared during the combustion, and which he called 'fire air.' To test this conclusion, he essayed to decompose heat by bringing it in contact with some substance which was supposed to have a great affinity for phlogiston, in the hope of removing its 'phlogiston' and liberating its 'fire air.' Such substances as 'fuming acid of nitre,' 'mercurial nitre,' or the 'red calx of mercury,' were therefore heated over a charcoal fire in a glass retort to the neck of which was fastened a bladder for the reception of the expected 'fire air.' In the case of the experiment with the mercury calx (red mercuric oxide) the anticipation was that:

$$\underbrace{\text{heat}}_{\text{‘fire air’} + \text{phlogiston}} + \text{mercury calx} \quad \textit{would react giving} \quad \underbrace{\text{mercury}}_{\text{calx} + \text{phlogiston}} + \text{‘fire air’}$$

Scheele thus isolated 'fire air' (oxygen), and found that by adding it to the inert 'residual air' left in his combustion experiments ordinary air could be regenerated, which proved, he said, "that ordinary air consisting of two kinds of elastic fluid, can be compounded again after these have been separated from each other by means of phlogiston."

On 1st August, 1774, Priestley, who believed that all discoveries are made by chance, tried one of his 'random shots' in an endeavour to extract air from red oxide of mercury ('*mercurius calcinatus per se*') by concentrating the sun's rays upon it with a burning glass, by which means he found that "air was expelled from it very readily." What surprised him most (he says) was that "a candle burned in this air with a remarkably vigorous flame . . . very much like that enlarged flame with which a candle burns in nitrous air, exposed to iron or liver of sulphur . . . and a piece of red-hot wood sparkled in it, exactly like paper dipped in nitre. . . ." Indeed it appeared to support combustion more vigorously than even the 'dephlogisticated nitrous air' (nitrous oxide) which he had discovered some years previously. At first he seems to have considered it to be "nothing more than such kind of air as I had brought nitrous air by the processes above mentioned," but in the following year he became fully satisfied that the new air was not 'dephlogisticated nitrous air' but ordinary air which had been completely dephlogisticated. Hence he called it 'dephlogisticated air,'—a very pure kind of air—observing that though it "might be very useful as a medicine it might not be so proper for us in the usual healthy state of the body; for, as a candle burns out much faster in dephlogisticated than in common air, so we might, as may be said, *live out too fast*, and the animal processes be too soon exhausted in this pure kind of air. A moralist, at least, may say, that the air which nature has provided for us is as good as we deserve."

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* It is interesting to note that Scheele entirely disbelieved the notion of phlogiston having a *negative* weight, and therefore the property of making things lighter by uniting with them; on the contrary he regarded it as a *Substance* "which always supposes some weight. . . ."

Priestley also devised a method for estimating the 'goodness' (*i.e.* oxygen-content) of air, by means of 'nitrous air' (nitric oxide), and so founded the art of gas analysis. The results obtained in this way by himself and others were, however, so discordant that the opinion became current that the composition of air varies according to locality and season of the year; and the instrument used for such determination of the quality of air was called a eudiometer (*i.e.* fine weather measurer), a name by which it is still known.

The constancy of the composition of air was, however, first established by Henry Cavendish who, in the year 1781, analysed with great care samples of it which had been taken in various localities. He found that all the samples had the same composition, namely (as he put it), "the quantity of pure air in common air is 10/48"; in other words, according to him, 100 volumes of common air invariably contain 20·8 volumes of 'dephlogisticated air' (*i.e.* oxygen) and 79·2 of 'phlogisticated air' (*i.e.* inert gases). When it is recalled that the most refined modern analyses shew 20·96 of oxygen to 79·04 of nitrogen, etc., we see how accurately Cavendish worked with the instruments available 150 years ago.

Another prevalent notion which Cavendish's researches dispelled was that 'fixed air' (carbon dioxide) is always produced when an inflammable substance is burnt in air; he found such to be so only when either charcoal or some animal or vegetable substance, but not when either sulphur or phosphorus, is so burnt.

In July 1781 Cavendish first made his discovery of the composition of water, although he did not publish it until three years later. In conjunction with his friend Warltire, Priestley had previously observed a condensation of water on exploding a mixture of 'inflammable air' (hydrogen), and either common or 'dephlogisticated' air in a copper globe of about three pints capacity. The condensed liquid had a bluish colour and contained copper nitrate. They concluded, however, that the water formed in such experiments had pre-existed in the original gases, and had mostly been condensed out of them after the explosion; for Priestley had, as he said, long entertained the opinion "that common air deposits its moisture by phlogistication." They also thought that the process had involved a loss in weight.

Cavendish, who saw more clearly the importance of the matter, at once set himself to ascertain the cause of the water formation, and found that "when inflammable air and common air are exploded in a proper proportion, almost all the inflammable air, and near one-fifth of the common air, lose their elasticity, and are converted into dew. And by this experiment it appears that this dew is plain water, and consequently that almost all the inflammable air, and about one-fifth of the common air, are turned into pure water." Also, he recorded that although the vessel used held 24,000 grains of water, and "though the experiment was repeated several times with different proportions of common and inflammable air, I could never perceive a loss of weight of more than one-fifth of a grain, and commonly none at all. . . ." He next proceeded to examine the nature of the matter condensed on firing a mixture of dephlogisticated and inflammable airs, for which purpose he exhausted with an air-pump "a glass globe holding 8800 grain measures, furnished with a brass cock and an apparatus for firing air by electricity." He then admitted into it a mixture of 19,500 grain measures of dephlogisticated air and 37,000 of inflammable air. On subsequently shutting the cock and firing the included mixture by electricity "almost all of it lost its elasticity," so that on opening the cock again more of the same mixture entered to supply the place of that destroyed by the explosion; this was again fired, and the operation repeated till almost the whole of the mixture was let into the globe and exploded. Finally he proved, what he had always suspected, that the production of nitric acid in such experiments was "no essential part of the dephlogistication" by shewing that if the proportion of dephlogisticated air used "be such that the burnt air is almost entirely phlogisticated, the condensed liquor is not at all acid, but seems pure water, without any addition whatever . . ." from which it follows "that almost the whole of the inflammable and dephlogisticated air is converted into pure water." From these experiments Cavendish concluded "that dephlogisticated air is only water deprived of its phlogiston, and that inflammable air . . . is either phlogisticated water, or else pure phlogiston; but in all probability the former," adding that "there is the utmost reason to think that dephlogisticated and phlogisticated air, as M. Lavoisier and Scheele suppose, are quite distinct substances, and not differing only in their degree of phlogistication; and that common air is a mixture of the two. . . ."

It was Lavoisier, however, who first realised that the discoveries of

Black, Priestley, Scheele and Cavendish were incompatible with the old theory of phlogiston; and, using their discoveries supplemented by his own experiments, he finally overthrew it and established his oxygen-theory of combustion. It was apparently during the course of a correspondence with Black, whom he called his master and teacher, that he first began to suspect the validity of the old theory. In 1772 he commenced to experiment for himself on combustion, and found that when sulphur and phosphorus are burnt, so far from there being any loss, a great increase in weight occurs. This recalled the observations of Jean Rey, as long ago as 1630, that metals increase in weight on calcination. Lavoisier therefore concluded that a large quantity of air becomes fixed in combustion; and, in order to confirm this view, he reduced litharge with charcoal, finding that a large amount of air was liberated. In 1774 he calcined lead and tin in closed vessels containing air, shewing that so long as the vessel remained closed no change in weight occurred, but that when the vessel was subsequently opened, air rushed in, and the weight increased. Also, he found that only a portion of the enclosed air was taken up by the molten metal, the residual air being inert. He thus seems to have arrived at the conclusion that common air is composed of two different gases, of which one is active and the other inert in combustion.

In October 1774 Lavoisier heard from Priestley, who was then visiting Paris, of his discovery of 'dephlogisticated air' and its wonderful properties, at which Lavoisier "expressed great surprise." He had presented in 1774 a paper to the French Academy entitled "*Opuscules physiques et chimiques*," in which *inter alia* he discussed the subject of combustion; but it was not published until 1778, by which time he had revised and extended it. In 1775, after he knew of Priestley's work, he spoke, in a further paper "*Sur la combustion en général*" before the Academy, of the "principle which unites with metals during calcination," and in 1778 he spoke of the '*l'air pur*' or '*l'air vital*,' which he now proposed to call '*oxigene*' ('acid producer'), as the constituent of the air which combines with sulphur, phosphorus or charcoal during combustion to yield acids, or with metals to form calces.

In 1776-7 he shewed that a diamond burns forming 'fixed air' (carbonic acid gas) only, and that when organic products are burnt, 'fixed air' and water are produced; also that when phosphorus is burnt in a closed vessel one-fifth of the air contained therein is used up, the residual air being inert. For a time, however, Lavoisier was impeded by his then belief that acid substances must be produced by the combustion of a non-metal, and by his failure to detect any acid formed in the combustion of hydrogen.

He satisfied himself that the new gas obtained by Priestley and Scheele from mercury calx is really the active part of the atmosphere in combustion by an ingenious experiment in which 4 ounces of pure mercury were heated to near the boiling point in a retort communicating with a bell-jar and trough in such-wise that the system contained 50 cub. inches of air confined over mercury. For a few hours no perceptible change occurred, but on continuing the heating red specks began to appear on the bright surface of the hot mercury, and gradually increased in number and size until after some days no further change was observable. After 12 days the heating was stopped, and the apparatus allowed to cool down to the room temperature, when it was found to contain between 42 and 43 cub. inches only of gas instead of the 50 cub. inches originally. Some 45 grains of red calx were collected from the surface of the mercury, and on subsequently strongly heating them in a small glass tube connected with a graduated cylinder full of water inverted in a pneumatic trough they decomposed yielding 41½ grains of mercury and between 7 and 8 cub. inches of oxygen.

In 1783, after Cavendish's discovery of the composition of water, Lavoisier correctly interpreted its compound nature as an oxide of hydrogen and boldly published his *Reflexions sur le phlogistique,* in which he denied the existence of phlogiston and propounded his new oxygen-theory of combustion. His main contentions were that (1) inflammable substances will burn only in oxygen or where oxygen is present, (2) oxygen is consumed in combustion, and, uniting with the substance burnt, causes an increase in its weight and a corresponding decrease in the weight of the air used, and (3) the combustible substance is thereby usually converted into an acid, although metals are converted into their calces.

Throughout his researches Lavoisier assumed axiomatically the principle of the conservation of mass. For, as Ernst von Meyer has said, he "was penetrated by the truth that no matter is lost during chemical reactions; what many others accepted as being correct, without emphasising it particularly, was for him a law upon which he based his speculations and researches." * He made the balance the *ultima ratio* of the laboratory, and it was his unfailing insistence upon this principle that finally secured the triumph of his antiphlogistic theory. Moreover, in conjunction with Laplace, he founded the science of thermo-chemistry by enunciating the principle that as much heat is required to resolve a chemical compound into its constituent elements as is evolved in its formation from them. The phlogistonists generally had regarded heat as a ponderable material; but by shewing that substances may be burnt in closed vessels without any diminution in weight, Lavoisier disproved so false a notion and prepared the way for the mechanical theory of heat.

His '*matière de chaleur*' had no weight, and science owes to Laplace and him the earliest attempts to determine experimentally heats of combustion by means of a calorimeter, and the first experimental evidence of the conservation of energy in combustion.

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* *History of Chemistry,* p. 159.

In 1789, when Lavoisier published his *Traité Elementaire de Chimie—présenté dans un ordre nouveau et d'après les découvertes modernes*—in which he reinterpreted the principal facts of chemistry in terms of his antiphlogistic oxygen theory—his views were rapidly gaining ground ; and before his death by the guillotine during the ' Reign of Terror ' in 1794 they had been all but universally accepted. Black, who lived until 1799, frankly accepted it ; Scheele had died in 1786 in the old faith ; Cavendish, who remained unconvinced, had virtually retired from scientific controversy. Priestley alone remained in active opposition, and it happened that he was not long in discovering a fact which for a while greatly embarrassed the antiphlogistonists.

In 1776 an inflammable gas, now known as carbonic oxide, had been obtained by Lassone by heating zinc calx with charcoal ; and although Lavoisier subsequently obtained it by heating together alum and charcoal, and had proved it to form ' fixed air ' in combustion, it was for a long time confused with hydrogen, on the supposition that the charcoal used in obtaining it had contained that element. In 1796 Priestley obtained the same gas by heating together iron scale (oxide) and charcoal, both of which had been previously so well calcined that there could be no question about their substantial freedom from both water and hydrogen. According to the antiphlogistonists, however, the experiment ought to have yielded carbonic acid gas, and not an inflammable air at all. Priestley further added to their discomfiture by shewing that an inflammable air (now called ' water gas ') is also obtained when steam is passed over red-hot charcoal, which (he said) proved the gas to be ' phlogisticated water ' as the phlogistonists had maintained. So, in 1800, he hurled these facts with great gusto at his adversaries in his last chemical publication, *The Doctrine of Phlogiston Established*. But his victory was short lived ; for the ink had hardly dried on his script before Cruikshank shewed experimentally that the inflammable air obtained by heating carbon with metallic oxides burns forming only carbonic acid, without any trace of water, using up in the process less oxygen than is contained in the product. He therefore called it "gaseous oxide of carbon." Somewhat later Clément and Désormes confirmed his results, and further shewed that the gas may also be produced by passing a stream of carbonic acid gas over incandescent charcoal, thus shewing it to be a lower oxide of carbon. And so the controversy ended in the complete vindication of the oxygen theory.

CHAPTER III

DALTON'S EXPERIMENTS ON THE PARTIAL COMBUSTION OF MARSH AND OLEFIANT GASES

Until the year 1776 no distinction was drawn between 'inflammable airs' from different sources; in that year Volta discovered that the gas issuing from marshes (marsh-gas) differs from that obtained by dissolving certain metals in dilute acids (hydrogen) in requiring four times as much oxygen (by volume) for its combustion, and yielding carbonic acid as well as water as the result thereof. In 1785 Berthollet confirmed the fact that marsh gas contains both carbon and hydrogen, and the distinction between the two 'inflammable airs' soon became recognised universally.

It was not, however, until Cruikshank's work in the year 1800 that carbonic oxide was distinguished from hydrogen; or until 1805 that 'marsh gas' was distinguished from the 'olefiant gas' obtained by the action of sulphuric acid upon alcohol, both being then regarded merely as compounded of carbon and hydrogen. In that year, however, William Henry of Manchester proved that the gases obtained by the destructive distillation of coal contain two distinct gaseous 'carburetted hydrogens,' namely a 'light carburetted hydrogen,' identical with 'marsh gas,' and a 'heavy carburetted hydrogen,' identical with 'olefiant gas.' This distinction was subsequently independently confirmed experimentally by Dalton, Davy, and Berzelius. The last named proposed the name 'elayl' for olefiant gas, and it subsequently was called ethylene; the name methane was given to 'marsh gas' by Hofmann at a much later date.

During the years 1803 and 1804 John Dalton studied closely the composition of the two carburetted hydrogens, finding that the lighter one ('marsh gas') contains just twice as much hydrogen to a given quantity of carbon as the other ('olefiant gas'). Certainly this relationship had become clear to him by 24th August, 1804, because an examination in 1896 by Roscoe and Harden of his laboratory note-books brought to light the following entry under that date: *

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* *A New View of the Origin of Dalton's Atomic Theory*, Roscoe and Harden (1896), p. 63.

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	Olefiant Gas.		
Meas.	*Acid.*	*Oxy.*	*Dimin.*
100	200	300	200
	Stagnant.		
100	100	200	200

All gases containing olefiant are distinguished by the smell: the oxycarbonate * and stagnant † not."

Accordingly, in a Table of the more correct Specific Gravities, etc., of Certain Gases, dated 14th September, 1804, in his note-book, Dalton represented 'Carb. hyd. from water' as a compound of 1C+2H and 'Olefiant gas' as a compound of 1C+1H, clearly shewing that by this time he had visualised them in terms of his atomic theory, which he had first outlined in papers and lectures in Manchester and London during 1803–4.

In his *System of Chemistry*, published in 1807, Thomas Thomson, who spent a day or two with Dalton in Manchester in August 1804, said: "Mr. Dalton informed me that the atomic theory first occurred to him during his investigations of olefiant gas and carburetted hydrogen gas, at that time imperfectly understood, and the constitution of which was first fully developed by Mr. Dalton himself," a statement which for long was accepted generally by chemists as indicative of the origin of Dalton's atomic theory. The aforesaid investigation of Dalton's laboratory notebooks, etc. by Roscoe and Harden, however, has shewn conclusively that it was "the atomic theory which helped to clear up the existing confusion about the composition of carburetted hydrogen, and not the analysis of the gas which led to the atomic theory." Indeed, it is now clear that it was from the physical rather than the chemical standpoint that Dalton approached his atomic theory.

In his *New System of Chemical Philosophy*,‡ published in 1807, Dalton used the results of his eudiometric analyses of marsh gas and olefiant gas to illustrate his law of multiple proportions which was the logical outcome of his atomic theory. And, in addition, he disclosed the following remarkable experiments which he had carried out on the explosion of each of these gases with defect of oxygen. Strangely enough, these experiments seem to have been overlooked by his contemporaries; else it is hard to believe how the dogma of the preferential combustion of the hydrogen of hydrocarbons, which was universally held by chemists during the greater part of the nineteenth century, could ever have taken root.

On exploding a mixture of marsh gas with its own volume of oxygen in a eudiometer over mercury Dalton found some formation of steam, but the cooled products, which occupied nearly the same volume as the original gases, consisted mainly of equal volumes of carbonic oxide and hydrogen, as though the partial combustion had taken place in accordance with the equation:

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* The '*oxycarbonate*' gas = "in reality a compound of gas oxid of carbone and hydrogen in equal parts."

† The '*stagnant*' gas = carburetted hydrogen from stagnant water = marsh gas.

‡ Part ii. p. 442.

$$CH_4 + O_2 = CO + H_2O + H_2.$$

He described the experiment as follows: "If 100 measures of carburetted hydrogen be mixed with 100 measures of oxygen (the least that can be used with effect), and a spark passed through the mixture, there is an explosion, without any material change in volume; after passing a few times through lime water it is reduced a little, manifesting signs of carbonic acid. The residue is found to possess all the characters of a mixture of equal volumes of carbonic oxide and hydrogen. Upon adding 100 measures of oxygen to the residue and passing a spark nearly 100 measures of carbonic acid are produced, and the rest of the produce is water."

His experiment upon the explosion of ethylene with its own volume is so important from the point of view of the theory of hydrocarbon combustion that it is here recounted in his own words. "There are some remarkable circumstances attending the combustion of olefiant gas in Volta's eudiometer, which deserve notice as part of the history of the gas, but particularly as this puts the constitution of the gas beyond doubt. If 100 measures of oxygen be put to 100 of olefiant gas and electrified, an explosion ensues, not very violent; but instead of a diminution, as usual, there is a great increase of gas (instead of 200 measures there will be found about 360); some traces of carbonic acid are commonly observed, which disappear on passing two or three times through lime water; there will remain, perhaps 350 measures of permanent gas, which is all combustible, yielding by an additional dose of oxygen carbonic acid and water, the same as if entirely burnt in the first instance. What, therefore, is this new gas in the intermediate state? It is carbonic oxide and hydrogen mixed together, an equal number of atoms of each. One third of the oxygen requisite for the complete combustion suffices to convert the carbon into carbonic oxide, and the hydrogen at the instant is liberated; hence the other two thirds are employed, the one to convert the carbonic oxide into acid, the other the hydrogen into water. In fact the 350 measures consist of nearly 170 of each gas, which together require nearly 170 of oxygen for their combustion."

Thus did the great Manchester chemist inform his contemporaries that when ethylene is exploded with its own volume of oxygen, its carbon is burnt to carbonic oxide and its hydrogen liberated, in accordance with the equation:

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

It seems strange that so decisive an experiment, published in one of the great classics of chemistry, should have been ignored until the same fact was re-discovered in 1891 in H. B. Dixon's laboratories at the Owens College, Manchester, when its importance was instantly recognised; still more so that for two-thirds of the nineteenth century a theory of hydrocarbon combustion quite incompatible with it should have universally prevailed. Such, however, was the case, a striking example of how a scientific discovery of first importance may long be neglected, whilst a theory at variance with it is exalted almost into an unquestionable article of faith.

CHAPTER IV

HUMPHRY DAVY'S RESEARCHES ON FLAME
1815 TO 1819

Invention of the Miner's Safety Lamp

SIR HUMPHRY DAVY's researches on flame were carried out at the Royal Institution in London during the years 1815 to 1819, in response to an appeal from a Society formed two years previously in Sunderland for Preventing Accidents in Coal Mines, in consequence of a disastrous explosion which had occurred on 25th May, 1812, at Felling Colliery near Jarrow, involving the loss of ninety-two lives. The direct outcome of these experiments was his invention of the Miner's Safety Lamp; but they also so greatly extended our knowledge of flame and explosions generally that they are rightly regarded as having laid the foundations of almost all subsequent investigations upon the subject. They were published in his *Collected Works*, vol. vi. pp. 3–130 (1840), which were edited by his brother John Davy.

He began by analysing six samples of firedamp which had been collected and forwarded to him by Matthias Dunn from a blower at Hebburn Colliery (Co. Durham), and shewing the combustible part thereof to consist of 'marsh gas' (methane), as Dr. William Henry had previously stated. He also found this to be (as he said) "much less combustible than other inflammable gases. It was not exploded or fired by red hot charcoal or red hot iron; it required iron to be white hot, and itself in brilliant combustion, for its inflammation. The heat produced by it in combustion was likewise much less than that of most other inflammable gases, and, hence, in its explosion, there was much less comparative expansion," which statement, however, requires qualification in the light of present-day knowledge.

He next proceeded to shew that the range of explosibility of mixtures of the gas with air is comparatively narrow; for, when mixed with three or four times its bulk of air it extinguished a taper, but exploded feebly with between five and six times its own volume of air. Its most violently explosive mixture was one with between seven and eight times its own volume of air. On further dilution it retained its liability to explosion until the proportion of air was fourteen times its own volume, after which limit a lighted taper could be plunged in the mixture without producing any explosion, its flame being merely enlarged, an effect which could be observed until a proportion of one volume of the gas to thirty volumes of air was reached. In this way Davy defined the explosibility of marsh gas-air mixtures as lying between the limits of 1 of gas to between 5 and 6 of air, and of 1 of gas to about 14 of air, respectively, which are not far from those now recognised.

He thus brought to light two important facts, namely : (1) that a given inflammable gas has certain definable limits of explosibility in admixture with air (or oxygen), and (2) that there are differences between the 'ignitibilities' of such explosive mixtures of various inflammable gases with air.

From such observations, and others, he deduced that a certain 'heat' (*i.e.* temperature) is required for the ignition of any particular inflammable gas-air mixture, and that unless after ignition such heat is passed on continuously from one layer of the mixture to the next there cannot be continuous propagation of flame through it. Hence, he concluded that by sufficiently cooling such an explosive mixture it should be possible to prevent the passage of flame through it in the event of some local ignition occurring. And, on putting the matter to the test of experiment, he found that an explosive mixture of inflammable gas and air could be cooled below its ignition temperature, either by dilution with an inert gas or by contact with the walls of narrow tubes, especially if they were made of good heat-conducting material. It was such reasoning, verified by experiment, which led him to design his well-known Miner's Safety Lamp, as will now be explained.

Having discovered that metal tubes were more effective than glass in preventing the passage of flame through explosive mixtures contained therein, he proved that " a mixture of the gas with air would not explode in metallic canals or troughs when their diameter was less than $\frac{1}{7}$ of an inch, and their depth considerable in proportion to their diameter ; nor could explosions be made to pass through such canals " ; also, that " explosions would not pass through very fine sieves or wire gauzes."

Accordingly, in a paper read before the Royal Society on 9th November, 1815, " On the fire-damp of coal mines, and on methods of lighting the mines so as to prevent its explosion," Davy stated that " it is only necessary to use air-tight lanterns, supplied with air from tubes or canals of small diameter, or from apertures covered with wire gauze placed below the flame, through which explosions cannot be communicated, and having a chimney at the upper part, or a similar system for carrying off the foul air ; . . . and common lanterns may easily be adapted to the purpose, by being made air-tight in the door and sides, by being furnished with the chimney, and the system of safety apertures below and above." And three lamps constructed on such principles were described in the paper.

In a further paper read before the Royal Society on 11th January, 1816, entitled "An account of an invention for giving light in explosive mixtures of fire-damp in coal mines by consuming the firedamp," Davy announced his discovery that flames protected by a wire-gauze cylinder of a sufficiently fine mesh might be carried quite safely into an explosive mixture of fire-damp and air. For (he said) "on plunging a light surrounded by a cylinder of fine wire gauze into an explosive mixture, I saw the whole cylinder become quietly and gradually filled with flame; the upper part of it soon appeared red-hot; yet no explosion was produced." His invention therefore consisted "in covering or surrounding the flame of a lamp or candle by a wire sieve; the coarsest that I have tried with perfect safety contained 625 apertures in a square inch, and the wire was $\frac{1}{70}$ of an inch in thickness, the finest 6400 apertures in a square inch, and the wire was $\frac{1}{250}$ of an inch in thickness." *

A lamp constructed on this new principle was successfully tested on 9th and 17th January, 1816, in an explosive atmosphere down the Hebburn Colliery. Mr. Buddle, the manager, who was present, afterwards wrote: "It is impossible for me to express my feelings at the time when I first suspended the lamp in the mine, and saw it red-hot; if it had been a monster destroyed I could not have felt more exultant than I did. I said to those around me, 'We have at last subdued this monster'." †

It should here be said that Davy's great contemporary George Stephenson, who was then an engine-wright at Killingsworth Colliery, near Newcastle-on-Tyne, and had independently studied the problem, simultaneously invented a similar "safety lamp" to that of Davy, using a fine wire gauze to prevent the flame from igniting an explosive atmosphere outside. This led to a controversy between their respective supporters as to which of the two inventors had priority; but though it may be difficult to decide such a point, for they were independently working at the same time at the problem, and produced similar solutions of it almost simultaneously, we may say that whilst Stephenson worked by rule of thumb without any knowledge of chemical principles and deserved the greatest credit for his invention, Davy not only solved the immediate problem, but also by his scientific researches discovered and defined the principles underlying the safety of mines from fire-damp explosions which all subsequent investigators have confirmed and followed.‡

The Nature of Flame and Cause of the Luminosity of Flames

Davy defined flame as "aëriform or gaseous matter heated to such a degree as to be luminous," and whilst believing that it might be produced independently of any chemical change, as is shewn (he said), "in the discharge of voltaic electricity through an undecomposable gas," he regarded the flame of combustible bodies as in all cases "the combustion of an explosive mixture of inflammable gas or vapour and air; for it cannot be regarded as a mere combustion at the surface of the inflammable matter." This constituted the first clear recognition that, so far as combustion is concerned, the appearance of flame implies the continuous burning of an explosive mixture.

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* For fire-damp he recommended a gauze of iron wire from $\frac{1}{40}$ to $\frac{1}{60}$ inch in diameter, with 784 apertures to the inch, as the best; but he pointed out that for more inflammable gases finer gauzes should be employed.

† *Minutes of Evidence, Select Committee on Accidents in Mines, 1835.* Question No. 2226.

‡ A full account of the "History of the Safety Lamp" is given in a paper published by F. W. Hardwick and L. T. O'Shea in *Transactions of the Institution of Mining Engineers*, vol. 51, (1915-16) p. 548, to which the reader is referred.

On reflecting upon an observation that "when a wire-gauze safety-lamp is made to burn in a very explosive mixture of coal gas and air, the light is feeble, and of a pale colour; whereas the flame of a current of coal gas burnt in the atmosphere . . . is extremely brilliant," Davy tells us that he was "led to imagine that the cause of the superiority of the light of the stream of coal gas might be owing to the decomposition of a part of the gas towards the interior of the flame where the air was in smallest quantity, and the deposition of solid charcoal, which, first by its ignition, and afterwards by its combustion, increased in a high degree the intensity of the light," and that a few experiments soon convinced him that this was the true explanation. He was thus led on to the general conclusion that the luminosity of flames is caused "by the production and ignition of solid matter," which, he said, would explain the intensity of the light of the flame of phosphorus or of zinc burning in oxygen as compared with "the feebleness of the light of those flames in which gaseous and volatile matter alone is produced, such as those of hydrogen and sulphur in oxygen, or of phosphorus in chlorine, etc." For, he continued, "whenever a flame is remarkably brilliant and dense, it may be always concluded that some solid matter is produced in it; on the contrary, when a flame is extremely feeble and transparent, it may be inferred that no solid is formed."

In this connection it should be noted that, although there is perhaps a latent ambiguity in Davy's attribution of the separation of carbon in a hydrocarbon flame to "the decomposition of a part of the gas towards the interior of the flame where the air was in smallest quantity," nowhere did he expressly say that it is due to a preferential combustion of the hydrogen, a view which sometimes has been credited to him. Such a doctrine, though irreconcilable with Dalton's experiments on the partial combustion of methane and ethylene described in the previous chapter, sprang up soon after Davy's death, and seems to have been countenanced by Faraday; * but it is doubtful whether Davy ever held it.

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* *E.g.* Lecturing at the Royal Institution in 1860-1 upon "The Chemistry of a Candle," Faraday said, "The volatile matter raised by combustion from the tallow of a candle is a vapour composed of carbon and hydrogen . . . the forces which hold these elements together are so nicely balanced that the hydrogen is made to combine first, the carbon afterwards."

Effects of Rarefaction and Dilution upon Flames and Explosions

Davy made many experiments with the object of determining what degrees of rarefaction or dilution, respectively, are necessary to extinguish the flames of various combustible gases. With regard to rarefaction, on general grounds he had formed the opinion that amongst combustible gases " those which require least heat for their combustion ought to burn in more rarefied air than those that require more heat, and those that produce much heat in their combustion ought to burn, other circumstances being the same, in more rarefied air than those that produce little heat," and he considered that his experiments, which resulted as follows, supported this conclusion. He found that in the same apparatus :

Hydrogen	ceased to burn in air	at between	$\frac{1}{7}$ and $\frac{1}{8}$	atmospheric	pressure.
Carbonic oxide	,,	,,	$\frac{1}{6}$	,,	,,
Marsh gas	,,	,,	$\frac{1}{4}$	,,	,,
Olefiant gas (ethylene)	,,	,,	$\frac{1}{10}$ and $\frac{1}{11}$	,,	,,
Sulphuretted hydrogen	,,	,,	$\frac{1}{7}$	,,	,,
Sulphur	,,	,,	$\frac{1}{20}$	,,	,,
Phosphorus	,,	,,	$\frac{1}{60}$	,,	,,

Similarly, he found that a mixture of hydrogen and oxygen in their combining proportions could not be exploded at ordinary temperatures by a spark at $\frac{1}{18}$ atmospheric pressure, although it could be so fired at that pressure when the containing vessel was heated to the softening point of glass. From this he argued " that expansion by heat, instead of diminishing the combustibility of gases, on the contrary enables them to explode, apparently, at a lower temperature, which seems perfectly reasonable, as a part of the heat communicated by any ignited body must be lost in gradually raising the temperature."

He made the following remarkable observations upon the effects of diluting electrolytic gas ($2H_2 + O_2$) with various gases on its ignitibility by means of " a strong spark from a Leyden jar " :

Inflammation of One Volume of Electrolytic Gas.

Occurred with	*but was prevented by*			
6	8	volumes	of	hydrogen.
7	9	,,	,,	oxygen.
10	11	,,	,,	nitrous oxide.
$\frac{3}{4}$	1	,,	,,	marsh gas.
$\frac{1}{3}$	$\frac{1}{2}$	,,	,,	ethylene.
$1\frac{1}{2}$	2	,,	,,	sulphuretted hydrogen.
$1\frac{1}{2}$	2	,,	,,	hydrogen chloride.

These results, he said, whilst they did not pretend to have a high degree of precision, shewed " that other causes, besides density and capacity for heat, interfere with phenomena. Thus nitrous oxide, which is nearly $\frac{1}{3}$ denser than oxygen, and which, according to De la Roche and Berard, has a greater heat capacity in the ratio of 1·3503 to 0·9765 in volume, has lower powers of preventing explosion ; and hydrogen, which is fifteen times lighter than oxygen, and which in equal volume has a smaller capacity for heat,* certainly has a higher power of preventing explosion ; and olefiant gas exceeds all other gaseous substances in a much higher degree than could have been expected from its density and capacity." Indeed, it may be said that, although more than a century has elapsed since Davy made these experiments, very little attention has been paid to them.

Among other suggestive observations which he recorded in this connection may be mentioned (1) that electrolytic gas could be exploded by the spark even when diluted with five times its own volume of steam, and (2) that " even a mixture of air and carburetted hydrogen, the least explosive of all mixtures, required a third of steam to prevent its explosion, whereas a fifth of azote produced the effect."

Temperatures of Flames

On general grounds Davy concluded that the temperatures of flames " are probably very different " ; and he actually tried to determine the temperature of the flame produced by the explosion of cyanogen with twice its own volume of oxygen in the following interesting manner : " Cyanogen and oxygen, in the proportion of 1 to 2, detonated in a tube of about two-fifths of an inch in diameter, displaced a quantity of water which demonstrated an expansion of fifteen times their original bulk. This would indicate a temperature of above 5000° Fahrenheit, and the real temperature is probably much higher ; for heat must be lost by communication to the tube and the water." The great interest of this statement lies in the fact that it describes the first attempt ever recorded to estimate the temperature of a flame, and foreshadows much modern work upon the subject.

Discovery of Catalytic Combustion

During the course of his experiments Davy discovered in 1817 that combustible gases will combine slowly with oxygen at temperatures below their ignition points. Thus he wrote :

" I made various experiments on explosions, by passing mixtures of hydrogen and oxygen through heated tubes ; in the beginning of one of these trials, in which the heat was much below redness, steam appeared to be formed without any combustion. This led me to expose mixtures of oxygen and hydrogen in tubes, in which they were confined by fluid fusible metal, to heat; and I found that, by carefully applying a heat between the boiling point of mercury, which is not sufficient, and a heat approaching the greatest heat that can be given without making glass luminous in darkness, the combination was effected without any violence and without any light." *

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* Davy was, of course, wrong in this supposition, the molecular heat capacities of hydrogen and oxygen at 15° C. and constant pressure being nearly equal (6·82 and 6·96 cals. respectively).

The accuracy of these observations may be judged from the fact that, according to modern experiments (V. Meyer, H. B. Dixon and W. A. Bone) electrolytic gas may be kept in closed glass vessels at 350° C. for many days or even weeks without any measurable combination occurring, whilst even at 400° C. some days would necessarily elapse before it could be noticed. The temperature at which glass would just begin to be 'luminous in darkness' is about 500° C., and Davy was perfectly correct in estimating that the slow combination of hydrogen and oxygen at measurable velocity begins at some point between that temperature and 360° C.

This led him to make a further experiment in order to try whether the temperature of such slow combination, being lower than that required to produce flame, might yet be high enough to make solid bodies incandescent. In other words, Davy set out to enquire whether "seeing that the temperatures of flames far exceed those at which solids become incandescent, a metallic wire can be maintained at incandescence by the combination of gases at its surface, without actual flame."

Thereupon he tried the effect of introducing a warm platinum wire into a jar containing a mixture of coal-gas and air rendered non-explosive by excess of the combustible. The wire immediately became red-hot, and continued so until nearly the whole of the oxygen had disappeared. He thus discovered the well-known phenomenon of catalytic or surface combustion which has been the subject of so much recent investigation.

He tried similar experiments with mixtures of air and ethylene, carbonic oxide, hydrogen, or hydrogen cyanide, respectively, finding that, with a platinum wire of given thickness, the effect was more intense in hydrogen than in ethylene, and in ethylene than in carbonic oxide mixtures. In the case of mixtures of cyanogen and oxygen the platinum wire became white-hot, and yellow vapours of nitrous acid were formed; also, in the case of a mixture of ethylene rendered non-explosive by an excess of inflammable gas much carbonic oxide was formed. And the truth of his remark that "the chemical changes in general produced by slow combustion appear worthy of investigation," although not sufficiently realised then, has been abundantly proved during the present century.

With regard to his experiments upon catalytic combustion Davy recorded how he had succeeded in repeating the phenomena with a palladium

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* He estimated the temperature to be 1035° F. (=555° C.).

wire, but failed to do so with wires of silver, gold, iron, copper or zinc, He said, however, that Sementini, then Professor of Chemistry at Naples, had presented him in 1819 with a lamp " in which alcohol burnt without flame, by means of fine coils of silver wire, and afforded phenomena exactly of the same kind as the lamp furnished with wire of platinum." And, in reference to Döbereiner's discovery that finely divided spongy platinum, precipitated from solution, is capable of effecting the combination of hydrogen and oxygen at ordinary temperature, he said how he himself had " cooled the spongy platinum to 3° of Fahrenheit, and it still inflamed hydrogen nearly of the same temperature, issuing from a tube cooled by salt and ice."

He did not think that the true explanation of the phenomena in question is to be found in the supposition that spongy platinum either absorbs hydrogen or contains oxygen, but rather that it will be found to be an electro-chemical one ; for he said :

" Supposing oxygen and hydrogen to be in the relation of negative and positive, it is necessary, to effect their combination, that their electricities should be brought into equilibrium or discharged. This is done by the electric spark or flame, which offers a conducting medium for this purpose, or by raising them to a temperature in which they become themselves conductors. Now, platinum, palladium and iridium are bodies very slightly positive with respect to oxygen ; and though good conductors of electricity, they are bad conductors and radiators of heat ; and, supposing them in exceedingly small masses, they offer to the gases the conducting medium necessary for carrying off and bringing into equilibrium their electricity without any interfering energy, and accumulate the heat produced by this equilibrium. Other metals do not possess the same union of qualities, yet most of them assist combination at lower temperatures than glass, which is a non-conductor of electricity."

It may be that the present generation of physical chemists does not appreciate fully the significance of Davy's views upon the phenomena in question; but time and the steady accumulation of new facts, will shew how much truth is contained in them. For chemical students generally, there is no better model of logical experimental procedure, accurate reasoning, philosophical outlook, and fine literary expression than Davy's papers on flame.

CHAPTER V

EXPERIMENTAL WORK ON CATALYTIC COMBUSTION
1819 TO 1836

DAVY'S discovery of catalytic combustion stimulated several of his contemporaries to investigate the subject, and during the next fifteen years a good deal of attention was paid to it. In 1819 Döbereiner discovered that spongy platinum, prepared by the ignition of ammonium platinochloride, is so exceedingly active in promoting the union of oxygen and hydrogen that it will ignite a mixture of the gases at as low a temperature as 0° C., and the well-known Döbereiner lamp as a convenient means of producing fire (' friction matches ' not being invented until 1827 *), was a practical outcome of his researches. He also found that freshly prepared ' platinum black ' absorbs oxygen from the air, and acquires the power of forming steam when plunged into a jar of hydrogen. On re-exposure to the air such power is renewed, and the operation can be repeated several times, the metal ' absorbing ' oxygen and carrying it over to the combustible gas. Iridium, osmium and palladium in a spongy condition were found to behave likewise at low temperatures.†

Dulong and Thénard also made systematic investigations, finding that the activity of platinum in any particular case varies not only with its physical state but also with its previous environment. Thus, whereas previous free exposure to air at ordinary temperature was found to diminish its activity, keeping it in a closed vessel hardly affected it; its activity was lost more quickly in damp than in dry air, but could be restored by either ignition or treatment with nitric acid and subsequent drying at 200° C. Other metals than those of the platinum group were found to have the power of inducing the slow combination of electrolytic

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* The first inventor of "Friction Lights" (as he called them) was undoubtedly John Walker, an apothecary, of Stockton-on-Tees, who in 1825 compounded a "percussion powder" of equal parts by weight of potassium chlorate and antimony sulphide; such mixture (made into a paste with gum) was afterwards used for the tips of "Friction Lights" made and sold by him from 7th April, 1827, onwards, as recorded in his Day-Book, which one of us (W. A. B.) examined some years ago.

† Döbereiner, *Schw.* **34**, p. 91; **38**, p. 321; **39**, p. 159; **42**, p. 60; **63**, p. 465; also *Gilb. Ann.* **74**, p. 264.

gas; thus gold in thin leaf acted at 260° C., but when precipitated from its solution by zinc, and afterwards ignited, it became active at as low a temperature as 55° C. Silver, similarly precipitated by zinc, was found to be much less active, requiring a temperature of 150° C. Non-metallic substances such as charcoal, pumice-stone, porcelain, rock crystal and broken glass were found to become active at about 350° C.[*]

In 1825 William Henry observed that when a warm platinum ball was immersed in a mixture of equal volumes of electrolytic gas and ethylene the hydrogen alone was burnt, none of the hydrocarbon disappearing unless the original mixture contained a larger proportion of oxygen,[†] a result which was afterwards confirmed by Thomas Graham.[‡] This led the Italian physicist Fusinieri to advance the theory that the power possessed by metals of inducing gaseous combustion is conditioned by a condensation or occlusion of the combustible gas (and particularly of hydrogen) at the surface, whereby it is rendered more than ordinarily active.

Faraday studied the retarding effects of various gases upon the combustion of electrolytic gas in contact with platinum foil, finding that the smallest effect was exerted by nitrous oxide, followed by hydrogen, nitrogen, air, and finally oxygen, in the order given. Turner also made similar experiments, finding that the addition either of one-third volume of carbonic oxide, or of one-tenth volume of sulphuretted hydrogen, to one of electrolytic gas rendered the action feeble even on the application of heat.[§]

The mechanism of such catalytic combustion was the subject of a celebrated controversy between Faraday and De la Rive in 1834–5. De la Rive held the view that it consists in a series of rapidly alternating oxidations and reductions of the surface, citing in support thereof the fact that when an alternating current is passed through acidulated water in an electrolytic cell with platinum electrodes, both of them become coated with a fine dust produced, as he said, by repeated oxidation and reduction of the surface; also, he urged Döbereiner's experiments with platinum black (*q.v.*) as supporting evidence.[||]

Faraday, on the other hand, contended that the function of the surface is to condense both the oxygen and the combustible gas, thus producing in the surface layers a condition comparable to that of high pressure. Against this view it was urged that, whereas such condensation should diminish, the catalytic action of the metal increases as the temperature rises. It is interesting to note also that Faraday had observed the combustion of hydrogen and oxygen over a cold platinum surface to be inhibited by the presence of small quantities of carbonic oxide, olefiant gas or ether, but he formed no definite opinion as to the reason, which, 'remains to be decided by more extended experiments.' No crucial experimental evidence distinguishing between the chemical and physical theories was forthcoming at that time, and when the controversy finally died out in 1836 interest in the subject suddenly dropped and was not revived for sixty years.

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[*] Dulong and Thénard, *Ann. Chim. Phys.* **23**, 446; **24**, 380; also *Gilb. Ann.* **76**, 83, and *Schw.* **40**, p. 229.

[†] *Ann. Phil.* **21**, p. 364, and **25**, p. 416.

[‡] *N. Quart. Journ. of Sci.* **6**, p. 354.

[§] Faraday, *Experimental Researches on Electricity*, i. p. 165; *Phil. Trans.* 1834, i. 55; *Pogg. Ann.* **33** (1834), 149.

[||] De la Rive, *Pogg. Ann.* **46** (1839), 489, 492; **54**, 386, 397; *Ann. Chim. Phys.* **39**, 328.

Although Faraday's unparalleled genius as an experimentalist was chiefly exercised in directions other than that of combustion, his famous lectures on "The Chemical History of a Candle," delivered, in 1848-9 and again in 1860-1, to a juvenile audience at the Royal Institution, London, are so exquisitely lucid in style and treatment that they serve for all time as a model of how a chemical subject should be expounded in public.

CHAPTER VI

THE BUNSEN ERA

1836 TO 1880

Bunsen's Method of Gas Analysis

THE period 1836 to 1880 may be justly named 'the Bunsen Era,' because it was dominated by the influence of that great chemist and his pupils, whose researches will now be reviewed.

It was in the year 1836 that Bunsen, on his appointment as Lecturer in Chemistry at the Polytechnic School of Cassel, began his researches into the quantitative analysis of gases, whereby he brought methods—depending upon either their selective absorptions by suitable reagents or their explosion with a suitable excess of air or oxygen—into such perfection that he may be said to have established a new chemical art on lines which left little room for subsequent improvement. In this connection special mention should be made of his discovery that the formation of oxides of nitrogen in explosion analyses may be avoided by dilution of the theoretical 'detonating gas' (*e.g.* $2H_2+O_2$) with twice its own volume of excess oxygen or air, a precaution which, although often neglected, is essential to accuracy. His principal work on gas analysis and combustion was embodied in his well-known *Gasometrische Methoden* (1857 and 1877), an English translation of which was made by his pupil H. E. Roscoe.

In 1838 he applied his methods to the investigation of the gases issuing from the iron-smelting blast furnaces in Veckerhagen, the results of which were published a year later.* In 1844–5, in conjunction with his pupil Lyon Playfair, he similarly investigated the gases evolved from a blast furnace at Alfreton in Derbyshire, and the Report thereon which he and Playfair made to the British Association in 1845 † is justly regarded as constituting one of the greatest advances in scientific metallurgy. It shewed, by the careful analysis of the gases at various levels in the blast furnace, not only how the chemistry of the smelting operation may be elucidated but also how its energy balance sheet may be drawn up. It should also be recalled that it was the exact experiments of Bunsen and

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* *Pogg. Ann.* 46 (1839), p. 97.

† *British Assoc. Report* (Cambridge), 1845.

Schischkoff upon the compositions of the products of the explosion of gunpowder, etc., which provided a basis for a theory of its combustion.

The Invention of the Bunsen Burner

The story of how Bunsen came to invent, in the year 1855, his well-known atmospheric gas-burner, cannot better be told than in the following words of an eyewitness, Sir Henry E. Roscoe, who at the time was one of his pupils in Heidelberg :

" Some short time before the opening of the new laboratory the town of Heidelberg was for the first time lighted with gas, and Bunsen had to consider what kind of gas-burner he would use for laboratory purposes. Returning from my Easter vacation in London I brought back with me an Argand burner with copper chimney and wire gauze, which was the form commonly used in English laboratories at the time for working with a smokeless flame. The arrangement did not please Bunsen in the very least, the flame was flickering, it was too large, and the gas so much diluted with air that the flame temperature was greatly depressed. He could make a burner in which the mixture of gas and air would burn at the top of the tube without any gauze whatsoever, giving a steady flame, under conditions such that it not only would burn without striking down when the gas supply was turned on in full, but also when the supply was diminished until only a minute flame was left. This was a difficult, some thought impossible, problem to solve, but after many fruitless attempts, and many tedious trials, he succeeded, and the ' Bunsen burner ' came to light." * It may be recalled that Bunsen never patented it, or undoubtedly he would have made a fortune by it ; but, as Roscoe said, " the notion of making money out of his discoveries, or of patenting any of them, never entered his head."

A great deal of controversy subsequently took place as to why the luminosity of a coal-gas flame (which was then much greater than nowadays, owing to the gas then being richer in heavy hydrocarbons C_nH_{2n} and benzene vapour) is destroyed when it is partly aërated before combustion as in the Bunsen burner. Davy's view that the luminosity of a hydrocarbon flame is due to the separation therein of solid particles of carbon, though at times challenged, held its own, and is now universally accepted. A crucial experiment made by the late Sir George Stokes, in which the image of the sun was focussed on to the flame and the scattered light when examined by a Nicol prism was found to be polarised, finally proved the presence of solid particles in the flame. The only debatable question now is the nature of the processes whereby the carbon particles are formed, whether they can be regarded as in all cases involving merely the thermal decomposition of certain hydrocarbons, or whether sometimes

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* Extracted from the Bunsen Memorial Lecture before the Chemical Society on 29th March, 1900 (*Trans. Chem. Soc.* 77, p. 547).

'partial oxidation' may also be concerned. The further discussion of this matter must be reserved, however, to later chapters, when recent work on flame reactions will be dealt with. For the present it will suffice to say that experiments made during the period now under discussion by Blockman, Knapp, Wibel and other investigators showed that in the Bunsen flame probably both dilution and oxidation co-operate in destroying the luminosity which is manifested when the primary air supply is cut off.

Bunsen's Experiments upon the Division of Oxygen between Hydrogen and Carbonic Oxide

In 1853 Bunsen undertook a series of experiments to test the validity of the Law of Mass Action propounded in Berthollet's *Essai de Statique Chimique* (1805), according to which if a substance A present in defect interacts with two or more substances B, C, etc., with each of which it can combine, the relative amounts of AB and AC produced when equilibrium is established in the system will be proportional to the products of the 'relative affinities' a_1 and a_2 of A for B and C, respectively, into the 'active masses' m_b and m_c of B and C, respectively, thus :

$$\frac{AB}{AC}=\frac{a_1 m_b}{a_2 m_c}.$$

His experimental method consisted in exploding in a eudiometer over mercury mixtures of electrolytic gas ($2H_2+O_2$) with varying amounts of carbonic oxide and determining the resulting ratio CO_2/H_2O in the cooled products. According to the Law of Mass Action this ratio should undergo a *continuous* increase with decreasing proportions of carbonic oxide in the mixture exploded, whereas Bunsen obtained the following results, which seemed to indicate a *discontinuous* alteration and a tendency for the oxygen to be divided between the combustible gases so as to produce hydrates of carbonic acid : *

TABLE I.—SHEWING THE RESULTS OF BUNSEN'S EXPERIMENTS

Experiment.		I.	II.	III.	IV.	V.	VI.	VII.	IX.
Volumes in mixture exploded	O_2	100	100	100	100	100	100	100	100
	H_2	200	200	200	200	200	200	200	200
	CO	793·8	575·0	448·6	294·7	174·0	119·3	80·7	74·0
Ratio CO_2/H_2O in products -		2·0	1·0		·5	·333		·25	·167

In another experiment (VIII.), where the mixture exploded contained $O_2=100$, $H_2=370·3$, and $CO=315·1$, the ratio CO_2/H_2O found was ·25, or the same as in VII.

* Liebig's *Annalen*, 85 (1853), p. 137.

Bunsen concluded that Berthollet's Law of Mass Action does not apply to gaseous explosions, but that:

"If the particles *a* of a homogeneous mixture have the choice of combination between the particles *b* and *c* of two other gases present in excess, a certain equilibrium ensues between the attractions of all the particles, so that the compounds $(a+b)$ and $(a+c)$, formed by the union of *a* with *b* and *c*, respectively, stand in simple relation to one another, dependent upon the amount of the particles remaining uncombined, and undergoing discontinuous alteration on gradual increase of these particles."

Thus was introduced the erroneous idea, which continued for a generation but has now been discarded, of there being a discontinuity in gaseous combustion, or, in other words, that it proceeds *per saltem*. For Bunsen averred that "the quantities of compounds which, under favourable circumstances, form simultaneously in a perfectly uniform gaseous mixture, bear simple atomic relations under sudden alteration by the gradual addition of a third body, which does not affect the homogeneous nature of the mixture." In 1874 E. von Meyer made similar experiments, obtaining results which he regarded as supporting Bunsen's theory.

It is not easy to account for the ratios CO_2/H_2O obtained by Bunsen in these experiments being as they were; but they undoubtedly accentuated the then prevailing scepticism concerning Berthollet's doctrine and retarded its general acceptance amongst chemists. Some years after Guldberg and Waage's revival and re-modelling of it in 1867, the division of oxygen in explosions between carbon monoxide and hydrogen present in excess was reinvestigated by both H. B. Dixon and Horstmann independently, who found that it took place in accordance with the principle of mass action; and it is now recognised that Bunsen's experiments were in one important respect defective, namely, in that he worked with a wet eudiometer. So that, but for their historical interest, they should now be disregarded. Indeed, the fact that Bunsen did not dry out his system at the outset of each experiment, and that therefore there would be an unknown and variable proportion of extraneous steam (one of the reaction products) present during such explosions, quite vitiated the results as a test of the principle of mass action. And in this connection it should be mentioned, that whereas in Experiments I., III., V. and VIII., the explosive mixtures were fired at a room temperature of between 22·3 and 23° C. and at pressures of between 720 and 740 mm., in Experiments II., IV., VI., VII. and IX. the temperature was always much lower (namely, between 2·3 and 7·0° C.), and the pressure also (namely, between 320 and 450 mm.). There would thus be about 2 per cent. by volume of steam present in the gaseous medium at the moment of ignition in the latter series of experiments as against about 3 per cent. in the former; but the further amounts of it added to the system during the explosion by evaporation from the wet walls would be incalculable.

Bunsen's Measurements of Flame Speeds

In 1857 Bunsen made the first measurements recorded of the speeds at which flames are propagated through gaseous explosive mixtures. His experimental method consisted in lighting the explosive mixture issuing at known velocity from a tube through an orifice of known diameter in a metal plate; its velocity of flow was then gradually reduced until the flame just struck back through the orifice and ignited the mixture in the tube beyond it. In this way he found a velocity of 1 metre per sec. for a theoretical mixture of carbon monoxide and oxygen ($2CO+O_2$) and of 34 metres per sec. for electrolytic gas ($2H_2+O_2$) at atmospheric pressure and temperature. The method, although simple and useful enough in its day, is open to the serious objection that the metal walls of the orifice would exert a considerable cooling effect upon the flame, which also probably would be further cooled to some extent by dilution with the outside air as it issued therefrom. These two effects would combine to lower the velocity. Probably also turbulence effects, having an opposite tendency, would come into play. In any case, at best the method would give a rough indication only, and never an exact measurement, of the *initial* speed of flame propagation through a given explosive mixture; and it has been superseded long ago by other much more accurate methods.

Bunsen's Determinations of the Pressures developed in Gaseous Explosions

In 1867 Bunsen published the results of his investigations upon the pressures produced when mixtures of hydrogen or carbonic oxide with the theoretical proportion of oxygen or air for complete combustion are exploded in closed vessels.* His method consisted in firing the mixtures at atmospheric pressure in a stout glass tube, (Fig. 1), 8·15 cm. long and 1·7 cm. internal diameter (capacity = 18 c.c.), which was closed by a suitable valve, *d*, the load on which could be adjusted by moving the weight, *b*, along one arm of the lever (another fixed weight, *a*, on the opposite arm being used as a counterbalance) until the valve was just lifted when the explosion occurred. The mixture was ignited by a powerful spark passed along the axis of the glass tube, and it was assumed that under such conditions combustion would occur instantaneously, and adiabatically, throughout the whole medium. Indeed it was calculated that, assuming a flame-speed of 34 metres per sec., in the case of electrolytic gas ($2H_2+O_2$), the flame would require $\frac{1}{4000}$ sec. only to traverse the short distance between the point of ignition on the axis of the tube and the walls thereof.

For each particular mixture trials were made with the object of finding two positions of the weight, *b*, as close together as possible, such that with the one quiet combustion ensued without the valve being lifted, with the other it was lifted and a 'report' was heard. The mean between these two load-limits was assumed to be that required just to balance the actual pressure generated by the explosion. From this Bunsen then calculated what he thought had been the mean flame temperature in each case. His experimental results, and temperature calculations therefrom, were as follows :

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* *Pogg. Annalen,* **131** (1867), p. 161, and *Phil. Mag.* **34** (1867), p. 489.

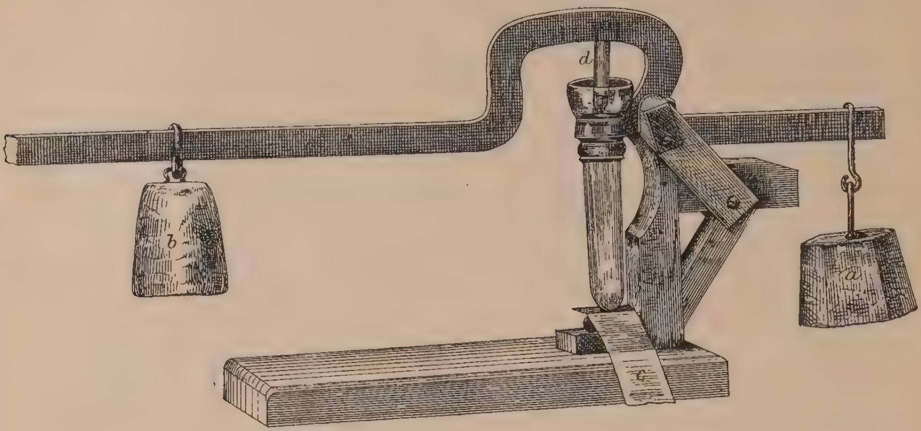

FIG. 1.—BUNSEN'S EXPLOSION APPARATUS.
(From the *Philosophical Magazine*, vol. xxxiv., 1867.)

TABLE II.—BUNSEN'S EXPERIMENTS ON THE PRESSURES DEVELOPED IN GASEOUS EXPLOSIONS

Mixture exploded at Atmospheric Pressure.	Limiting Load required for		Estimated	
	Quiet Combustion.	Lifting Valve.	Explosion Pressure.	Flame Temp.
	Atms.	Atms.	Atms.	°C.
$2H_2 + O_2$ - - -	9·56	9·46	9·46	2844°
$2CO + O_2$ - - -	10·20	10·04	10·04	3033°
H_2 – air (theoretical) -	—	—	7·50	2024°
CO – air (theoretical) -	7·34	7·22	7·30	1997°
C_2N_2 – air (theoretical)	11·01	10·90	10·95	—

The flame temperatures calculated for the theoretical $2H_2 + O_2$ and $2CO + O_2$ mixtures, respectively, happening to come out about one-third of those which he had expected (namely, about 8770° and 9020°, respectively)—on the supposition that the whole of the energy developed on explosion would be transferred without loss and appear as temperature in the products, whose specific heats were assumed not to vary with temperature, and for other reasons arising out of his H_2 – air and CO – air results, which need not be detailed—Bunsen concluded that the combustion had proceeded *per saltem*, one-third only of the gases having combined in the first instance. Thus, for example, in the case of the $2CO+O_2$ mixture, he supposed that one-third of it only had combined initially, whereby the mean temperature was immediately raised to 3033° C., but no higher; that the medium had then rapidly cooled to 2558°, at which a second burning occurred, the temperature remaining constant until one-half of the original mixture had combined; after which the remaining half underwent combustion as the temperature fell to 1146°, when the chemical change was completed.

The idea that gaseous combustion proceeds *per saltem*, in the manner indicated, thus received its credentials from Bunsen, and subsequently became widely accepted by chemists. Nevertheless, it was founded on assumptions, such as constancy of specific heats of products, which are now known to be wrong; moreover, Bunsen never made any allowance for energy directly radiated away from the flame, which does not appear as pressure (temperature) at all in an explosion. The further discussion of the matter will, however, be deferred until a later chapter, when the subject will be reviewed in the light of modern investigations. For the present it will suffice to say that the *per saltem* idea, though it died hard, is accepted no longer.

Landolt's Experiments upon the Order of Combustion in Coal-Gas Flames

In 1856 H. Landolt carried out experiments in Bunsen's laboratory to determine the order of the combustibilities of the principal constituents of coal-gas.* His apparatus (Fig. 2) consisted of the hollow brass cylinder, *AA*, 4·5 cm. high and 3·5 cm. diameter, with a circular opening, *BB*, of 7 mm. diameter, and a side tube, *C*, for the admission of coal-gas. A brass tube, *E*, was fitted along the vertical axis of the cylinder, leaving an annular opening at *BB*, at which the gas (previously freed from CO_2 and O_2) issuing from the cylinder *AA* was ignited, and making an air-tight joint with the bottom of the cylinder. A platinum tube, *DF*, drawn out at its upper end so as to form the narrow extension, *D*, terminating at *G* in an orifice of 1 mm. diameter, was inserted into *E* through an adjustable sliding joint at the bottom thereof. The lower end of *DF* was connected to an aspirator (not shewn in the diagram) through a weighed drying tube, so that the gases from any point along the vertical axis of the flame could be sucked off for analysis. The rate of flow of the coal-gas in each experiment was regulated so as to give a flame 10 cm. in height above the annulus at *BB*.

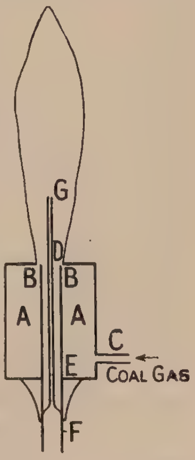

FIG. 2.—LANDOLT'S APPARATUS.

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* *Habilitations-schrift*, Breslau, 1856; and *Pogg. Annalen*, 99 (1856), p. 389.

No primary air supply was added to the coal-gas before it reached the said annulus, the whole of the air required for combustion being derived by diffusion from the atmosphere surrounding the flame.

In such manner, supplemented by careful analyses both of the coal-gas supplied to the flame, and of the gases sucked away therefrom at various vertical levels (*e.g.* at 0, 10, 20, 30, 40, 50, etc., mm. above the annulus *BB*), it was thought that the object of the investigation could be achieved. The results of a typical series of experiments are set out in Table III.

TABLE III.—LANDOLT'S RESULTS

Height of orifice *G* in mm. above annulus *BB* -	0		10		20		30		40		50	
Vols. air combining at *G* per 100 vols. gas -	27·08		45·43		172·76		227·73		335·30		381·66	
Vols. gas-air mixture combining at *G* - -	127·08		145·43		272·76		327·73		435·30		481·66	
Vols. of combustion products at *G* - -	111·41		120·09		245·96		311·37		422·59		461·23	
Composition of gas-air mixture (*a*) and flame gases (*b*) -	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Volumes of :												
Hydrogen -	39·30	22·66	41·04	14·95	44·00	5·49	44·00	15·54	41·37	14·50	41·37	11·95
Methane -	40·56	33·77	40·71	30·20	38·40	28·34	38·40	21·55	38·30	11·92	38·30	3·64
Carbonic oxide	4·95	7·34	7·64	14·07	5·73	14·05	5·73	14·58	5·56	22·24	5·56	25·14
Heavy hydrocarbons -	7·19	7·29	7·28	7·49	7·27	7·87	7·27	7·94	9·34	7·05	9·34	5·45
Oxygen - -	5·67	·66	9·52	·78	36·21	·47	47·73	—	70·28	—	79·99	—
Nitrogen -	29·41	29·41	38·66	38·66	140·78	140·78	184·23	184·23	270·45	270·45	307·10	307·10
Carbon dioxide	—	1·94	—	2·34	·37	10·11	·37	14·98	—	23·76	—	32·34
Steam - -	—	8·34	—	11·60	—	38·85	—	52·55	—	72·67	—	75·61

It should be observed that the coal-gas burnt was very rich in both heavy hydrocarbons and methane; and, assuming the heavy hydrocarbons on the average to have had the composition of propylene (C_3H_6), about 660 volumes of air would have been required for complete combustion of 100 volumes of the gas, from which the apparent degree of total combustion at each level in the flame may be judged by reference to the analytical results. Thus, at the 30 mm. level apparently it was about one-third, and at the 50 mm. level about 60 per cent. complete.

From a comparison between the composition of the gases sucked off through the platinum tube and those actually burnt at each level in the flame it appeared as though (1) the hydrogen had been burnt most rapidly in the lower part of the flame where the air supply was least, (2) the methane had disappeared at a fairly steady though less rapid rate throughout the flame, but (3) the heavy hydrocarbons remained intact until they reached the upper half of the flame. Landolt interpreted the results as meaning that in such flames the order of combustion of the various gases is (1) hydrogen, (2) methane, and (3) the heavy hydrocarbons, for he said : "*Die Gase verschwinden also nach dem Grade ihrer Verbrennlichkeit. Der Wasserstoff ist unter allen Gasarten diejenige welche am leichsten verbrennt, ist nimmt daher derselbe auch in der Flamme am schnellsten ab; etwas langsamer verschwindet das Grubengas, und zuletzt die schweren Kohlenstoffe, deren Verbrennung hauptsächlich erst in der oberen Hälfte der Flamme vor sich geht.*"

These experiments seemed so strongly to support the idea, which had prevailed since Davy's time, of hydrogen being the most combustible of all gases, that it became accepted as a proven fact, and held the field almost unchallenged during the next half century or so.

Nevertheless, in 1861, Kersten published the results of an experiment upon the explosion of a mixture of ethylene and electrolytic gas, which, had they been attended to, would have shaken men's faith in the dogma, for they not only contradicted it but pointed in a precisely opposite direction.* The mixture exploded was approximately of the composition $C_2H_4+3H_2+1\frac{1}{2}O_2$, and the results were as follows :

Original Mixture Exploded. c.c.		Gaseous Explosion Products. c.c.
$C_2H_4 = 5{\cdot}48$	yielded on explosion	$C_2H_4 = 0{\cdot}38$
$H_2 = 15{\cdot}40$		$CO = 10{\cdot}50$
$O_2 = 7{\cdot}70$		$H_2 = 20{\cdot}70$
$N_2 = 0{\cdot}22$		$N_2 = 0{\cdot}22$
Total = 28·80		Total = 31·80

It will be seen that, whereas 93 per cent. of the original ethylene had been burnt chiefly to carbonic oxide and hydrogen, as Dalton had found, at least two-thirds of the original hydrogen remained intact. Kersten did not fail to point out the moral, adding that, in hydrocarbon flames it would seem as though "before any portion of the hydrogen is burnt, all the carbon is burnt to carbonic oxide, and that the excess of oxygen divides itself between the carbonic oxide and the hydrogen." In 1874 E. von Meyer obtained results which in the main supported Kersten's view.

The results of modern research, which in due course will be dealt with, have entirely reversed Landolt's conclusion as regards the order of combustibility of hydrogen and hydrocarbons in flames. Indeed, we now see that in his experiments the sucking off of the gases from the flame through a narrow platinum tube, which would become red-hot when it was immersed in the flame, would bring catalytic actions into play sufficiently powerful to mask the real flame-reactions. Consequently, in all probability the products actually collected and analysed would not represent (as was supposed) those of the flame reactions, but rather those of a catalytic combustion, in which, as is now known, the hydrogen would be selectively burnt. All this shews how carefully all such experimental evidence should be scrutinised before being accepted at its face value.

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* *Journ. Prak. Chem.* 84 (1861), p. 310.

Deville's Researches upon Dissociation

The fact that steam can be decomposed at a white heat was first established by Sir William Groves in 1847, whose experiments formed the subject of the Bakerian Lecture of the Royal Society in that year.*

In 1857 Sainte Claire Deville commenced his classical researches upon the subject, and in 1864 he delivered two lectures before the Paris Chemical Society upon the results thereof, which were afterwards published separately under the title *Leçons sur la Dissociation*, in that year. He originated the term 'dissociation,' to denote the dissolution, through the agency of heat alone, of a composite molecule into two or more components, which if the temperature be allowed to fall will recombine to form the original molecule, the process being reversible at all temperatures. He expressed his meaning in the following words :

"When heat acts on any matter it produces a dilatation which is attributed to a force which has been named 'the repulsive force of heat.' By choosing suitable matter for the experiment, and raising the temperature sufficiently, the distance between the molecules can be increased to such a degree that they separate and pass into the elementary state. This is a spontaneous decomposition, in the sense that no chemical phenomenon intervenes. . . . This I have proposed to call the dissociation of compound bodies. . . ."

In order to prove such dissociation experimentally, Deville realised the necessity of removing the products thereof from the zone and influence of high temperature as quickly as possible, so as to minimise their recombination during the subsequent cooling. He therefore employed three methods, namely (1) separation of dissociated constituents by diffusion, (2) dilution of them by an inert gas, and (3) rapid cooling.

To demonstrate the dissociation of steam he employed the arrangement of two co-axial porcelain tubes, *AA* and *BB*, shewn in Fig. 3, the inner one being porous and the outer one glazed. Such arrangement was heated in a furnace to a temperature somewhere between 1100 and 1300° C., steam being passed through the inner tube, *AA*, whilst a current of carbon dioxide was passed through the annular space between the two tubes. A small fraction of the steam being decomposed into its elements in passing through the heated zone in *AA*, the resulting hydrogen diffused through the porous walls thereof much faster than the oxygen, so that a separation of them was effected. On passing the gas issuing from the annulus into a tube containing a solution of caustic alkali the carbon dioxide was absorbed, and the hydrogen,* etc., collected; whilst on passing the steam issuing from *AA* into a collecting vessel containing water it condensed, leaving the oxygen, etc., which it had carried over. There would thus result (i) gas from the annular space consisting principally of hydrogen, and (ii) gas from *AA* consisting principally of oxygen, and in the circumstances these were regarded as having been produced by the dissociation of steam in *AA*.

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* *Phil. Trans.* 1847, p. 1.

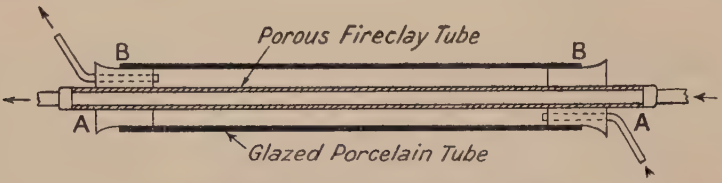

FIG. 3.—DEVILLE'S APPARATUS DIFFUSION METHOD.

The dissociation of carbon dioxide was proved by passing a slow current of the pure gas through a glazed porcelain tube packed with fragments of porous porcelain and heated in a furnace to 1300° C. The issuing gas was bubbled through a solution of caustic potash, and a residue collected which on analysis was found to consist of $CO=62{\cdot}3$, $O_2=30{\cdot}0$, and $N_2=7{\cdot}7$ per cent.

Finally, he proved the decomposition of carbonic oxide, in accordance with the equation $2CO \rightleftharpoons C+CO_2$, by the following 'hot and cold tube' method. The inner tube, *AA* (Fig. 4), of silvered copper was fixed co-axially within an outer tube, *BB*, of glazed porcelain, and the arrangement heated to bright redness in a charcoal furnace. A slow current of pure dry carbonic oxide was maintained through the annulus between the two tubes, whilst a stream of cold water was passed through *AA*. A small fraction of the carbonic oxide decomposed in passing through the heated zone of the annulus, depositing carbon on the cold outer surface of the silvered tube *AA*, and the presence of carbon dioxide in the exit gas was demonstrated by passing it through Liebig's bulbs containing a clear solution of barium hydroxide.

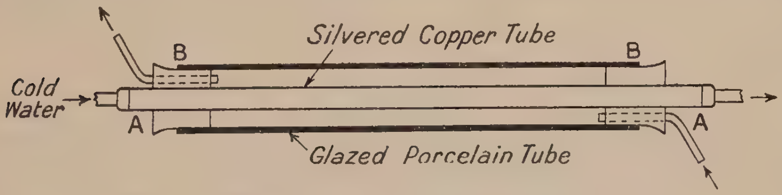

FIG. 4.—DEVILLE'S HOT AND COLD TUBE APPARATUS.

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* Probably there would be some CO also resulting from the reversible interaction $CO_2+H_2 \rightleftharpoons CO+H_2O$ in the heated zone.

Although such results may seem commonplace to present-day chemists, they were regarded with considerable wonder sixty years ago ; and it was soon recognised that the possible effects of ‘ dissociation ’ in gaseous combustion would have to be reckoned with. The further consideration of the matter must be deferred until a later chapter, when some of its quantitative and thermodynamical aspects will be dealt with.

Heats of Combustion

Throughout the period great progress was made in the science of Thermochemistry. In 1840 G. H. Hess enunciated the principle that the heat evolved in a chemical reaction is independent of the steps by which it is effected and of the order in which these steps succeed one another. Or, as Berthelot put it in his *Recherches de Thermochimie* (1865), the heat effect of a chemical change, when no outside work is done, depends only on the initial and final states of the system, and in no wise upon any intermediate stages. Berthelot also, in the same treatise, enunciated his ‘ principle of maximum work ’ to the effect that every chemical system strives after the attainment of the state of greatest stability, which is that giving rise to the greatest evolution of heat. In view, however, of the distinction which should be drawn between ‘ sensible heat,’ due to the kinetic energy of molecules, and ‘ radiation,’ due to their vibrational energy, it would perhaps be better to substitute ‘ energy ’ for ‘ heat ’ in the foregoing enunciations ; because, the total energy Σ liberated in (say) a given case of combustion comprises both that which appears as kinetic energy (pressure or temperature) of the products and that which is directly radiated away ; or,

$$\Sigma = k + r.$$

When, however, a substance is burnt in a water-cooled closed vessel, such as a calorimeter, the radiant-energy fraction r is absorbed and transformed into sensible heat by the walls, so that the whole of the energy emitted is measured by the sensible heat transmitted to and gained by the water.

Many eminent investigators devoted their attention to the exact determination of heats of combustion during the period, with the result that, before its close, data of unimpeachable accuracy had accumulated. Special mention should be made of the researches of Dulong (1830–40), Thomas Andrews (1848), Favre and Silbermann (1842–3), Berthelot (1875–9), and Julius Thomsen (1882–6).*

In 1879 Berthelot published in Paris his *Essai de Mechanique chimique fondee sur la Thermochimie* (2 vols.) embodying his principal experimental results, including a description of his new calorimetric bomb method. Julius Thomsen's *Thermochemische Untersuchungen* were published in four volumes between 1882 and 1886 ;* his results are generally regarded as being in all probability the most accurate available.

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* The reader is referred to a series of articles by S. Robson in the *Journal of Gas Lighting*, vol. cxxxii. (1915), pp. 431, 478, 532, 583 and 635, containing a detailed review of the methods employed and results obtained by these investigators.

According to Favre and Silbermann the heat of combustion of pure amorphous carbon, when completely burnt to the dioxide, is 8080 K.C.U. per kilogram. By means of their calorimetric bomb Berthelot and Petit found 8137·5 K.C.U. per kilogram for amorphous carbon, 7901 K.C.U. per kilogram for graphite, and 7860 K.C.U. per kilogram for diamond. The mean of Berthelot's and Thomsen's values would give 97·3 K.C.U. as the gram-molecular heat of formation of carbon dioxide from amorphous carbon. The following are Thomsen's results for the gram-molecular heats of combustion of the principal combustible gases and vapours when burnt at constant pressure to water and/or carbon dioxide at 18° C.

Julius Thomsen's Molecular Heats of Combustion

Gas.	K.C.U.	Vapours.	K.C.U.
Hydrogen	68·4	Benzene	799
Carbonic oxide	68·0	Toluene	956
Methane	212·0	Methyl alcohol	182
Ethane	370·5	Ethyl alcohol	340
Propane	529·0	Ethyl ether	660
Ethylene	333·3		
Propylene	492·7		
Acetylene	310·0		
Cyanogen	259·6		

It should be noted with regard to organic compounds, that an increase of CH_2 in ascending an homologous series corresponds with a constant increase of as nearly as possible 158·5 K.C.U. in the molecular heat of combustion.

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* *Vide* also Thomsen's *Thermochemistry*, trans. by Miss K. A. Burke (Longmans, Green and Co.).

CHAPTER VII

THE MODERN PERIOD

1880 TO 1926

A NEW era in combustion research was inaugurated in the year 1880 by the classical work of Mallard and Le Chatelier and of Berthelot and Vieille in France upon the initial stages of flame propagation and the development of detonation (' *l'onde explosive* ') in gaseous explosions, and by the equally important discovery by H. B. Dixon in England of the influence of moisture upon the combustion of carbonic oxide. These discoveries, following as they did upon the work of Clausius and Clerk Maxwell on the kinetic theory of gases, and the revival by Guldberg and Waage of the doctrine of mass action, with its thermodynamical implications were revolutionary in that they flooded the subject with new and unexpected light, and provided a new basis and *point d'appui* for further advance. The manifold problems presented by gaseous combustion and explosions were now considered *de novo* from the kinetic and thermodynamical, as well as from the chemical, points of view. New experimental methods were developed, stimulating enquiry in many directions. In England a new school of research arose at the Owens College, Manchester, under the leadership of H. B. Dixon, who moved from Oxford in 1886 to succeed Sir Henry Roscoe in the Chair of Chemistry in that famous institution.

As, however, the advances made during the period can best be described in a series of chapters, each dealing with a special aspect of the subject, we propose at this point of the narrative to change over from the historical to a systematic survey of it. Nevertheless, for those who may prefer the former method, in this chapter we will attempt to epitomise the most important advances which have marked the period, leaving the detailed consideration of them to the systematic part of our treatise.

The first decade of the period was ushered in by the brilliant work of the four French investigators referred to. This was marked by the application of photographic methods by Mallard and Le Chatelier to the investigation of the development and propagation of flame in explosive mixtures, and by the discovery of the phenomenon of detonation by them and by

Berthelot and Vieille simultaneously, revealing flame speeds far in excess of any previously contemplated, and comparable with the velocity of sound through gaseous media.

Mallard and Le Chatelier chiefly concerned themselves with the systematic investigation of phenomena associated with the initial stages of gaseous explosions up to the point when detonation is set up; they discovered and investigated (1) what has been termed the initial period of ‘uniform slow velocity’ in which the flame is propagated from layer to layer of the explosive mixture in an open tube ‘mainly by conduction,’ uninfluenced by compression waves or other accelerating causes, and (2) the ‘vibratory period’ which in certain definable circumstances intervenes between the said initial phase and that of detonation. The beautiful photographic method which they introduced and developed for this purpose constituted an entirely new and fruitful line of experimental attack, and is still being successfully applied to-day in research laboratories the world over.

Berthelot and Vieille not only discovered the development of ‘detonation’ in explosions, but were the first to devise and successfully apply a method for measuring accurately the high uniform flame speeds involved. Not only so, but Berthelot essayed the first theoretical exposition of the nature of what he termed ‘*l'onde explosive*,’ a problem of great intricacy which has since occupied the attention of several eminent mathematical-physicists, although it is not yet entirely solved. Berthelot likened the velocity of ‘*l'onde explosive*’ to that of a sound wave passing through the gaseous mixture, with, however, the important difference that, whereas a sound wave is propagated from layer to layer with a small compression and velocity determined solely by the physical condition of the vibrating medium, it is an abrupt change in chemical condition which is propagated in the explosion wave, and which generates an enormous force as it passes through each successive layer of the medium.

All the four French investigators successfully applied themselves to the determination of the pressures developed during gaseous explosions in closed vessels, a problem which had remained untouched since Bunsen's experiments in 1867. They confirmed his observations that the pressures realised fall far short of those calculated on the assumptions of adiabatic combustion conditions and constancy of the specific heats of the products; but they rejected his interpretation of the discrepancy, and ascribed it mainly to an increase in the specific heats of the products with temperature, which is now recognised as being a potent contributory cause.

The problem was also taken up in this country independently by Dugald Clerk, who, applying thermodynamical methods to the pressure-time curves, greatly advanced our knowledge of pressure-development in such explosions; and, while questioning the conclusion of the French investigators concerning increase in the specific heats of products with temperature, he suggested 'delayed combustion' as a probable contributory factor to the so-called 'pressure-suppression' in gaseous explosions. Later on he presided over a Committee appointed by the British Association in 1907 to investigate "Gaseous Explosions" from this point of view; and during the following five years it issued a series of reports, in which the problem was reviewed in the light of the great accumulation of knowledge and experience during the period now under review. The work of B. Hopkinson, W. T. David, Pier and Bjerrum, Tizard and Pye; and other engineers should also be referred to, in this connection.

It was in 1880 that H. B. Dixon, in repeating Bunsen's experiments on the division of oxygen between carbonic oxide and hydrogen, when both are present in excess, discovered that a mixture of carbonic oxide and oxygen, dried by long contact with phosphoric anhydride, would not explode when sparked in the usual way in a eudiometer over mercury, although the presence of even a trace of moisture at once rendered the mixture explosive. These experiments, proving as they did the complexity of what at first sight would appear to be one of the simplest cases of combustion, opened up an entirely new field of scientific investigation, and propounded questions of the highest theoretical importance which are still occupying the attention of chemists. H. B. Baker, one of Dixon's earliest pupils at Oxford, has gained such distinction in this particular field of work that the term 'Bakerian dryness' has acquired a special meaning, namely the most extreme condition of dryness and purity producible by any known means in a gaseous system. Baker's discoveries concerning the extreme inertness of many such systems to chemical change have raised fundamental issues, around which almost perpetual controversy has waged during the past forty years, but chiefly upon the question of whether or not the presence of steam is *essential* to combustion, either generally or in particular cases. This aspect of the problem will be discussed fully in a later chapter; but, in view more particularly of the recent work of W. A. Bone and his collaborators on the special cases of hydrocarbons and carbonic oxide, the correct answer to the general question would appear to be in the negative.

H. B. Dixon's work, as well as that of Horstmann, upon the division of oxygen between carbonic oxide and hydrogen in explosions, shewed, not only how Bunsen had erred unconsciously in using a wet eudiometer in his experiments, but also that when extraneous moisture is excluded from the system, and precautions are adopted to prevent condensation of steam during the cooling of the products of explosion, the process takes place in accordance with the principle of mass action, the validity of which was thus confirmed.

H. B. Dixon's other principal investigations, which have extended uninterruptedly over a period of nearly fifty years, and are still continuing, have comprised (i) the systematic determination of 'rates of explosion,' in which he greatly extended the work of Berthelot and Vieille, (ii) the photographic analysis of explosion flames, in which he followed up and extended the earlier work of Mallard and Le Chatelier, and (iii) the determination of ignition temperatures of gaseous explosive mixtures.

The second decade of the period under review was marked by new discoveries and controversies concerning the structure and luminosity of flames and the mechanism of hydrocarbon combustion. The rediscovery (1892), in H. B. Dixon's laboratory in Manchester, of what originally Dalton had found concerning the explosion of ethylene with its own volume of oxygen, together with the simultaneous observations of Smithells and Ingle (1892) upon the inter-conal gas of hydrocarbon flames, and the work of Lean and Bone (1892) and of Bone and Cain (1895) upon the explosion of ethylene or acetylene, respectively, with less than its own volume of oxygen, gave the time-honoured doctrine of the 'preferential combustion of hydrogen' in hydrocarbon flames its death-blow. The mechanism of the combustion of hydrocarbons was afterwards systematically studied by W. A. Bone and his various collaborators (1902–1912), whose results proved it to involve essentially the 'hydroxylation' of the hydrocarbon molecule followed by secondary decompositions, according to temperature conditions, of the primary hydroxylated products. In the course of their researches it was also shewn that the affinities of methane, ethylene, acetylene (and presumably also other hydrocarbons) greatly exceed that of hydrogen for oxygen in flames and explosions.

The structure and chemistry of flames were investigated by Smithells and Ingle, who published their experiments in 1892, and simultaneously by N. Teclu, an account of whose work appeared somewhat earlier. These investigators devised a simple method of separating the cones of an aërated Bunsen flame; moreover, Smithells and Ingle studied in detail the composition of the interconal gases of various hydrocarbon flames as well as those of a cyanogen flame.

About the same time (1892) V. B. Lewes propounded an 'acetylene' theory of the luminosity of hydrocarbon flames which provoked a lively controversy during the next few years, and incidentally led to a much closer experimental study of the thermal decomposition of hydrocarbons than had previously been attempted. In 1896 F. Haber published some work on the decomposition of the higher paraffins in which he severely criticised Lewes' 'acetylene' theory, rejecting it as being untenable; a similar view of the matter was afterwards (1908) taken by W. A. Bone and H. F. Coward as the result of their detailed study of the thermal decomposition of the simple hydrocarbons methane, ethane, ethylene and acetylene.

The third decade saw a revival of interest in catalytic combustion, and the discovery by W. A. Bone and C. D. M'Court (1909) of new means of realising in a serviceable manner the phenomenon of 'flameless incandescent surface combustion,' with ordinary refractory materials as catalysts, has led to its being successfully applied in various domestic and industrial directions the world over. On the theoretical side much discussion has taken place around the question of how such surfaces act in catalytic combustion, without, however, any general agreement being reached. One school of thought regards ionisation and the thermionic emissions by and from incandescent surfaces as the principal factor, whilst another school considers it to be an 'adsorption' effect due to some special kind of orientation of the reactant molecules at and by the surface. The two views, however, are not necessarily exclusive. Attempts have also been made to revive the old theory of De la Rive that the cause lies in rapidly alternating oxidation and reduction of the surface. The principal workers in this field have been M. Bodenstein (1899 to 1903), W. A. Bone and his collaborators (since 1903), Langmuir (since 1916), and, more recently, D. L. Chapman (1925). The subject, of course, forms part of the wider field of catalysis generally, which numerous other investigators have successfully cultivated ; and it seems possible that no single general theory as to surface actions is capable of explaining all cases of catalysis, so that rival theories may not necessarily be mutually exclusive.

During the past fifteen years R. V. Wheeler and his collaborators have paid great attention to the measurement of the speeds of the initial uniform flame propagation through gaseous explosive mixtures. Applying, with certain refinements, the photographic method originally devised by Mallard and Le Chatelier, as well as a 'screen-wire' electrical method on similar lines to those of previous workers, they have corrected some errors in the earlier French results, and published new data and curves for a large number of combustible gas and air mixtures. They have also propounded a 'flame-speed' law for complex gas and air mixtures, but experimental evidence recently published by one of us, and also independently by A. G. White, does not support it. The limits of inflammability of a large number of gas-air mixtures have been carefully determined by Wheeler and his co-workers, and other considerable extensions of our knowledge have resulted from their researches.

During the same period much attention has been directed to the electrical ignition of gaseous explosive mixtures, chiefly as the outcome of W. M. Thornton's work, in which it was proved that for given sparking conditions (*e.g.* electrodes, type of discharge, voltage, etc.) a certain minimum spark energy is required to ignite a given explosive mixture, and the question has naturally arisen as to whether (or how far) ignition and flame propagation are conditioned by ionisation. In this connection the recent work of G. I. Finch (1926) on the combination of hydrogen and oxygen in the electric discharge seems to be of fundamental importance.

Since 1921, W. A. Bone, in conjunction first of all with the late W. A. Haward, and afterwards with D. M. Newitt and D. T. A. Townend, has published a series of memoirs upon *Gaseous Combustion at High Pressures*, in which the behaviour of hydrogen-air and carbonic oxide-air mixtures, on explosion in specially designed bombs at initial pressures up to 175 atmospheres, has been investigated and new factors brought to light. In particular, it has been proved that nitrogen exerts a peculiar retarding and energy absorbing influence upon the combustion of carbonic oxide at high pressures, apparently due to some 'resonance' effect. At all events, when excess of oxygen is present in a $CO—O_2—N_2$ mixture exploded at high pressures, the formation of nitric oxide always far exceeds that corresponding with a purely thermal equilibrium at the maximum flame temperature. This has brought into prominence the question, first propounded by F. Haber and J. E. Coates in their memoir *Über die Stickoxyd Bildung bei der Kohlenoxydverbrennung* (1909), whether the formation of nitric oxide in flames may not be fundamentally an electrical effect ("eine im Grunde electrische Erscheinung"), or perhaps more correctly in the case of carbonic oxide flames an 'activation-by-radiation' effect.

In this connection F. Häusser's work upon the technical synthesis of nitric acid by means of gaseous explosions (1922) should be mentioned, in which he found that in the explosion of CO-air mixtures at initial pressures of 3·5 atmospheres "the formation of nitric oxide was between 25 and 100 per cent. greater than in the case of coal gas-air mixtures, and this in spite of the fact that the relevant conditions, viz. explosion pressures, explosion temperatures and nitrogen content, were practically identical, and that the difference in the oxygen content was insufficient to explain the considerable difference in the formation of the nitrogen oxides which resulted; and he was inclined to attribute this circumstance to "the possibility of nitric oxide formation by rays of short wave length." Without, however, dogmatising on what is admittedly an abstruse matter, it would seem that, at least in the opinion of those who have studied it practically, the phenomenon in question is inexplicable on any purely thermal grounds, and is probably a question either of ionisation or radiation. In this connection should be mentioned some recent experiments by W. T. David (1925) upon the influence of infra-red radiation upon the rate of pressure development in gaseous explosions.

Finally, it may be said that, in common with every other branch of chemistry, the science of combustion is being profoundly influenced by the truly astounding advances which have been made in our knowledge of atomic structure, radiation, and other fundamentals, and that already there are signs of the new wine bursting the old skins. For, just as the advent of the kinetic theory of gases and thermodynamics towards the middle of last century changed men's outlook upon combustion, and impelled them to re-search and extend the knowledge of the previous generation, so now we are at the threshold of a new era which will assuredly be at least as prolific of new discoveries and interpretations as the one now closing. The progress of scientific discovery continually teaches us the truth of the ancient proverb that "It is the glory of God to conceal a thing; but the honour of Kings is to search out a matter."

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SECTION II

CHAPTERS VIII TO XVIII

THE INITIATION AND DEVELOPMENT OF FLAME AND DETONATION IN GASEOUS EXPLOSIONS

CHAPTER VIII

IGNITION TEMPERATURES

Pre-Flame Combustion

Chemical change may be determined in a gaseous explosive mixture at a much lower temperature than is required to develop flame in it. In 1885 H. B. Dixon kept electrolytic gas, sealed up in a stout glass bulb at atmospheric temperature and pressure, at about 350° C. for 1000 hours without being able to detect the formation of as much as 1 per cent. of steam.* In 1895 V. Meyer and Raum † studied the slow combination of the elements of electrolytic gas in sealed glass bulbs at temperatures between 300° and 578° C. At 300° sixty-five days elapsed before any steam formation could be detected; at 350° a very small amount of combination (between 0·5 and 1·9 per cent.) occurred in five days; while at 448° the combination was still very slow. Some years later, in similar experiments, W. A. Bone and R. V. Wheeler ‡ were quite unable to detect the slightest formation of steam from electrolytic gas within a week at 335°, and even at 400° there was, in most cases, no appreciable combination during that period. Much the same was also found to apply in the case of moist mixtures of carbonic oxide and oxygen in their combining proportions.

Mixtures of hydrocarbons and oxygen, in suitable proportions, are much more reactive in the circumstances referred to. Thus, in their researches upon the slow combustion of hydrocarbons, W. A. Bone and his collaborators § found that mixtures of methane (2 vols.) and oxygen (1 vol.), sealed up in borosilicate glass bulbs at atmospheric temperature and pressure, reacted very slowly at 300°, but at 400° quite quickly. Similarly, equimolecular mixtures of either ethane, ethylene or acetylene with oxygen were very reactive at 300°, and in some cases even at 250°. ||

Such slow combinations usually start as *surface effects only*, in the sense

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* *Nature*, 1st October, 1885.

† *Ber.* 28 (1895), p. 2804.

‡ *Trans. Chem. Soc.* 81 (1902), p. 539.

§ *Loc. cit.* pp. 546 to 549.

|| *Trans. Chem. Soc.* 85 (1904), pp. 698 to 710; and 1641 to 1654; 87 (1905), pp. 1234 to 1243.

that they are confined to the layers of gas in contact with the heated walls of the containing vessel; though if there be a sufficient accumulation of heat in the system to raise its temperature, the reaction may spread to the main body of the gas, and so occur homogeneously in the system.

In the case, for instance, of electrolytic gas, interaction in a glass vessel usually commences as a surface effect only, and is first appreciable after some days at temperatures between (say) 400° and 500°. In such circumstances the rate of combination would be far too slow to allow of any accumulation of heat in the system; but, on gradually raising the temperature, the rate of combination would increase until at length a point (say about 550° C.) would be reached when the rate at which heat is lost from the system (*e.g.* by conduction through the walls of the enclosure) is more than counterbalanced by the rate at which it is developed by the interaction. The reaction would thus become *self-propellant*; self-heating of the medium would begin; its temperature would continue to rise, and the rate of combination would be rapidly accelerated until ignition occurred and flame appeared.

It may here be recalled that, in his Presidential Address to Section B of the British Association in 1907, Professor A. Smithells * directed attention to the fact that in a number of cases a mixture of two flame-forming gases on being heated develops luminosity quite gradually, *pari-passu* with the chemical combination induced, and likened the phenomenon to the phosphorescent glow of phosphorus in air, which begins at 7° C., or much below the temperature of 60° C. at which the substance breaks into flame. He pointed out that many other combustible substances, such as sulphur, arsenic, the vapour of carbon disulphide, alcohol, ether and light-petroleum, exhibit similar 'phosphorescence' when gently heated in contact with air, and expressed the view "that, in fact, phosphorescent combustion is the normal antecedent to what we ordinarily call flame." For, he continued, "the change from phosphorescence to ordinary flame is not sudden, but the appearance of ordinary flame is the end point of a continuous, though rapid development." † And he defined the true temperature of ignition as that "at which the reaction proceeds at a rate just sufficient to overbalance the loss of heat by radiation, conduction, and convection from the burning layer of gases, so that the next layer is put in the same state, and steady combustion proceeds."

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* *British Association Reports,* 1907 (Leicester), p. 469.

† H. B. Dixon, however, is of the opinion that such a generalisation does not apply to all cases of ignition, saying that in the case of carbon disulphide change from the phosphorescent to the ordinary flame combustion is not continuous, except in the sense that the descent of a mountain might be described as continuous if one glissarded further down a snow slope at a uniform rate, and then suddenly fell over a precipice.

Modes of Ignition

Although the temperature at which such autogenous or self-propellant reaction begins in a given gaseous mixture is usually termed its 'ignition temperature' or 'ignition point,' it is not ordinarily a well-defined physical constant, being dependent on the way in which heat is conveyed to the medium and other circumstances. It is clear also that it does not necessarily correspond with the actual appearance of flame in the mixture; indeed, there is often a definite 'pre-flame period,' during which the reaction is self-propellant.

Various methods are commonly employed for igniting a gaseous explosive mixture. Thus, for example, it may be (*a*) brought into direct contact either with a flame or some incandescent surface, (*b*) passed into a sufficiently heated enclosure, (*c*) fired by adiabatic compression, or (*d*) ignited by a sufficiently powerful electric spark. It has long been recognised as highly important, from both the practical and theoretical points of view, that precise knowledge should be gained experimentally of the factors governing the ignition of a given explosive mixture in each case. Indeed, it may be said that a complete knowledge of such factors is essential to a proper understanding of flame propagation through explosive mixtures; hence some of the ablest experimentalists have devoted considerable time to the study of ignition phenomena.

The Experimental Determination of Ignition Temperatures

It is desirable, at this point, to safeguard ourselves against using loosely the term 'ignition temperature' or 'ignition point,' because it is frequently employed as though it pertained to a particular combustible gas instead of a particular combustible mixture of gas and air (or oxygen). Thus we ought not to speak of the 'ignition temperature of hydrogen,' but only of the ignition temperature of a given mixture of hydrogen and air (or oxygen), because each such mixture has a different ignition temperature under like physical conditions. Moreover, it should be borne in mind not only that the ignition temperature of any given explosive mixture varies with the pressure, but also that other factors of 'environment' may possibly operate in a subordinate degree.

Davy was the first to investigate the subject; he did not, however, go beyond placing certain gases in what he regarded as their order of increasing inflammability, namely: methane, carbonic oxide, hydrogen, and phosphine, although he gave 116° C. as the ignition point of the last named. In 1867 Bunsen endeavoured, from explosion experiments, to deduce certain ignition temperatures, *e.g.* 2116° C. for electrolytic gas, diluted with 3·65 times its own volume of hydrogen, and 857° C. when diluted with ten times its own volume of oxygen. Unfortunately, however, he imported assumptions into his calculations which since have been disproved.

Mallard and Le Chatelier's Determinations (1880)

It was not until Mallard and Le Chatelier published their experimental researches in 1880 * that a real beginning was made with the experimental determination of ignition temperatures. Below are given some of their results, from which they concluded that, in general, the dilution of a detonating gas with either nitrogen or one of its own constituents has but little influence upon its ignition temperature; thus, for example:

	°C.
(1)	
1 vol. $(2H_2+O_2)$	555°
Do. *plus* 1 vol. N_2	
Do. *plus* 1 vol. H_2	
Do. *plus* 1 vol. O_2	530°
Do. *plus* 1 vol. CO_2	580°
(2)	
1 vol. $(2CO+O_2)$	650°
Do. *plus* 1 vol. N_2	
Do. *plus* 1 vol. CO	
Do. *plus* 1 vol. O_2	
Do. *plus* 1 vol. CO_2	700°
(3)	
1 vol. (CH_4+20_2)	650°
Do. *plus* 2 vols. N_2	
Do. *plus* 2 vols. CH_4	

It should be mentioned here that Mallard and Le Chatelier, whose experimental method was to allow the explosive mixture to enter a vacuous porcelain vessel previously heated to a known temperature, observed delays up to 10 secs. between the moment of filling and the appearance of flame in the case of methane-air mixtures, but not in other cases.

The Work of the Victor Meyer School (1891–1900)

During the closing decade of the last century (1891–1900) a number of continental chemists, notably Victor Meyer and his pupils in Germany and Emich in Austria, endeavoured to determine experimentally the ignition temperatures of explosive mixtures of the commoner combustible gases with oxygen, but their efforts were largely frustrated by the considerable amount of pre-flame surface-combustion which undoubtedly occurred in their experiments before the temperature of the medium as a whole had been raised to the true ignition point. Their results are, therefore, chiefly of historic interest, and need only be mentioned here quite briefly.

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* *Compt. rend.* 91 (1880), p. 825; and *Annales des Mines,* 8, Sér. iv. (1883), pp. 289-295.

V. Meyer and F. Freyer * employed two experimental methods, the explosive mixtures being either led through a tube immersed in a bath of hot liquid or vapour maintained at a constant temperature, or sealed up at atmospheric temperature and pressure in glass bulbs which were then suddenly plunged into the bath. For temperatures below the boiling point of sulphur an oil bath was used ; at higher temperatures the vapours of boiling sulphur (448°), phosphorus sulphide (518°), stannous chloride (606°), zinc bromide (650°), and zinc chloride (730°) respectively were employed. In the case of each gaseous mixture trials were made to find two bath temperatures at the lower (*a*) of which the mixture never exploded, but at the higher (*b*) it always did. The following results were obtained :

TABLE IV.—MEYER AND FREYER'S IGNITION TEMPERATURE RANGES

Equivalent Mixtures of	I. Free Current.		II. Closed Bulb.	
	(*a*)	(*b*)	(*a*)	(*b*)
Hydrogen and oxygen	650°	730°	530°	606°
Methane and oxygen	650°	730°	606°	650°
Ethane and oxygen	606°	650°	530°	606°
Ethylene and oxygen	606°	650°	530°	606°
Carbonic oxide and oxygen	650°	730°	650°	730°
Hydrogen sulphide and oxygen	315°	320°	258°	270°
Hydrogen and chlorine	430°	440°	240°	270°

It thus seemed as though, except in the case of carbonic oxide and oxygen, an explosive gaseous mixture would ignite at a lower temperature when it is heated up in a closed vessel, so that its pressure increases, than when it is flowing freely at atmospheric pressure through a heated open tube ; but the surface/volume ratio of such a tube, as well as the rate of flow of the gaseous mixture through it, would doubtless have a considerable influence upon the ignition temperature. The experimental results were not precise enough to be of more than empirical value, *e.g.* as shewing the order of ignitability of such mixtures under the conditions referred to.

V. Meyer and A. Munch † also tried experiments in which ignition was effected in a glass vessel placed inside the bulb of an air thermometer heated in a metal bath ; a mixture of the combustible gas with the theoretical amount of oxygen for complete combustion was passed through a fine tube to the bottom of the vessel, where it issued at a jet. The

* *Zeit. Phys. Chem.* **11** (1893), p. 28.

† *Ber.* **26** (1893), p. 2421.

temperature at which explosion occurred was determined with the following results:

Mixture.	Temperature °C. (a)	Temperature °C. (b)
Methane and oxygen	656°	678°
Ethane and oxygen	605°	622°
Propane and oxygen	545°	548°
Ethylene and oxygen	572°	590°
Acetylene and oxygen	509°	515°

In 1900 Emich,* using V. Meyer's open tube method, obtained the following results:

Mixture.	Temperature Range.
$2H_2+O_2$	518–606°
$2CO+O_2$	650–730°
CH_4+2O_2	606–650°
H_2+Cl_2	240–270°

H. B. Dixon's Concentric Tube Method

It was not until H. B. Dixon and H. F. Coward † introduced their well-known 'concentric tube method,' in which the combustible gas and air (or oxygen) were separately heated to the temperature of the enclosure before being allowed to mix, that the potent influence of heated surfaces in promoting 'pre-flame' combustion was sufficiently eliminated to give much confidence in the accuracy of any experimental determinations of the ignition temperatures of gases at atmospheric pressure.

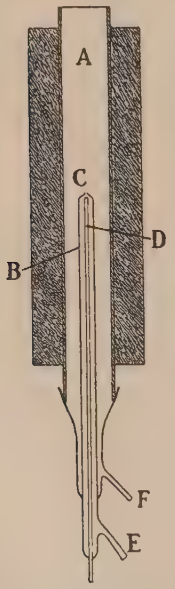

Fig. 5.—Dixon and Coward's Apparatus.

Their apparatus (Fig. 5) consisted of an electrically heated porcelain tube *A*, 45 mm. internal diameter, within which was fixed co-axially a narrower one *B*, terminating at its upper end in a fused quartz nozzle with an orifice *C*, whose diameter varied in different experiments between 0·6 and 2·1 mm. A fused platinum-platinum-iridium thermojunction *D*, situated immediately below *C*, and connected with an Ayrton-Mather dead-beat galvanometer, was used for measuring temperatures. In making an experiment the temperature of the tube *A* was gradually raised, usually about 5° per minute, from some 50° C. below the expected ignition temperature, the combustible gas and a supporter of combustion (air or oxygen) being supplied meanwhile, in separate streams through the side-tubes E and F respectively. The reacting gases were thus brought into contact at the temperature recorded at the thermojunction *without any previous mixing*. The temperature of each was thus slowly raised *pari-passu* until their admixture in the vicinity of the orifice resulted in flame. What actually was determined was a more or less narrow 'range of temperature' within which some one of the more favourable mixtures of the combustible gas and the air (or oxygen) would ignite at atmospheric pressure. The experimental results, which are given below, afforded no information as to the effect of varying the proportions of the gas and air (or oxygen) upon the ignition temperature.

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* *Monatsh.* 21 (1900), pp. 1061–1078.

† *Trans. Chem. Soc.* 98 (1909), p. 514.

TABLE V.—DIXON AND COWARD'S IGNITION TEMPERATURE RANGES

Combustible Gas.	Ignition Range.	
	In Oxygen (°C.).	In Air (°C.).
Hydrogen	580–590	580–590
Carbonic oxide	637–658	644–658
Acetylene	416–440	406–440
Ethylene	500–519	542–547
Methane	556–700	650–750
Ethane	520–630	520–630
Propane	490–570	—
Cyanogen	803–818	850–862
Hydrogen sulphide	220–235	346–379
Ammonia	700–860	—

It may be noted, in passing, that, whereas in some cases (*e.g.* hydrogen, carbonic oxide and acetylene) the observed ignition ranges were fairly narrow and practically the same for both oxygen and air, in others (*e.g.* methane and the paraffin hydrocarbons generally) they were much wider, and sometimes (methane) different in oxygen from in air. Also, that generally speaking, they were lower than those previously observed by V. Meyer and his pupils (*q.v.*) for equivalent mixtures of the corresponding gases with oxygen, a circumstance doubtless due in a large measure to the much greater elimination of 'surface' and 'pre-flame' effects in Dixon's experiments. Moreover, Victor Meyer's observation that the ignition ranges of paraffin hydrocarbon-air mixtures fall as the series is ascended was confirmed.

Influence of the Time-Lag

It has already been mentioned that Mallard and Le Chatelier had observed 'time-lags' between admitting their methane-air mixtures into a heated vacuous tube and the subsequent appearance of flame therein. In 1913 Taffanel and Le Floch shewed that similar time-lags occur in such circumstances with explosive mixtures generally.[*] More recently Mason and Wheeler,[†] in extending Taffanel and Le Floch's work, found 'lags' of considerable duration in cases of explosive mixtures of paraffins and air; thus, for example, a lag of 144 secs. was observed on admitting a 10·6 ethane/89·4 air mixture into a vacuous tube heated to 534° C.

In a recent paper reviewing his earlier experiments with H. F. Coward, H. B. Dixon has also directed attention to the importance of considering the question of 'lag' in connection with such determinations. For, as he rightly observes, when an explosive mixture is heated to its 'ignition point,' an appreciable time-interval may elapse before an actual appearance of flame. During such 'pre-flame' combustion the chemical changes which already have begun in the gaseous medium may be either quickened or retarded by various conditions in the environment. Accordingly, during recent years, he has been experimenting with an improved concentric tube apparatus, in which not only is the wall of the tube *A* further removed from the central orifice (Fig. 6) than in the former apparatus but also the 'lag' due to the pre-flame period can actually be measured. On trying an experiment with hydrogen in the new apparatus it at once became apparent that what Coward and he had formerly observed in the old apparatus was not the instantaneous ignition point, but that occurring after an interval of some 8 to 10 seconds. In the new apparatus hydrogen was found to ignite instantaneously (*i.e.* in less than 0·5 sec.) at 631°, whereas, with a 'lag' of 20 seconds, ignition occurred at 565° only. He then gave the following revised ignition temperatures, as determined in his new apparatus:

TABLE VI.—INFLUENCE OF 'LAG' ON IGNITION TEMPERATURE (DIXON)

Gas.	Lag. (sec.).	In Oxygen (°C.).	In Air. (°C.)
Hydrogen - -	0·5	625°	631°
	10·0	582°	588°
Carbonic Oxide -	0·5	667°	696°
	10·0	645°	668°
Methane - -	0·5	665°	725°
	10·0	624°	685°

In illustration of the effects of the 'lag' upon the observed appearance of flames ('ignition points') in such experiments, Dixon has recently cited

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[*] *Compt. rend.* 156 (1913), p. 1544; 157 (1913), p 469.

[†] *Trans. Chem. Soc.* 125 (1924), p. 1869.

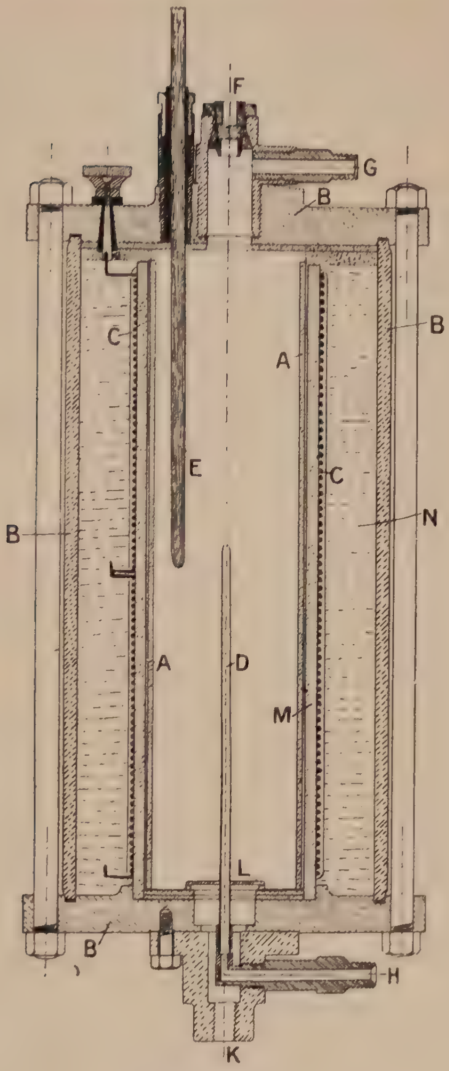

FIG. 6.—DIXON'S IMPROVED APPARATUS.

A. Glazed Silica Cylinder.
B. Steel outer case.
C. Electric heating wire.
D. Central tube of quartz.
E. Platinum Resistance Thermometer in Silica case.
F. Window.
G. Exit pipe leading to control valve.
H. Inlet for inflammable gas.
K. Inlet for air or oxygen.
L. Baffle Plate.
M. Clay Furnace-cylinder.
N. Kieselguhr packing.

the following determinations for carbon bisulphide vapour in his new apparatus :

Lag		0·5	1·0	2·0	3·0	5·0	7·0	10·0 secs.
Observed Ignition point.	*In oxygen*	132°	128°	123°	118°	114°	110°	107° °C.
	In air	156°	151°	145°	138°	130°	124°	120° °C.

It seems probable that such effects of ‘ lag ’ are primarily due to ‘ pre-flame ’ combustion producing heat more rapidly than it is dissipated, with the result that, if sufficient time be allowed, the temperature of the system is raised to that at which flame appears. In other words, the longer the time that can be allowed for the inflammation to occur, the lower is the temperature to which the gaseous medium need be heated in the first instance. Hence, for many practical purposes, the *minimum temperature* to which a particular mixture need be heated initially, in order to ensure eventual inflammation after an unlimited time interval, should be regarded as the effective ignition temperature rather than that to which it must be heated initially in order to ensure instantaneous inflammation. Indeed, for all ‘ safety ’ purposes, this should be so.

The following experimental results will suffice to illustrate further the influence of ‘ lag ’ upon the observed ignition temperatures in Dixon's new concentric-tube apparatus :

TABLE VII.—INFLUENCE OF ‘ LAG ’ ON IGNITION TEMPERATURE. RECENT DETERMINATIONS (DIXON)

(*a*) *Ignition Temperatures of Hydrogen at Atmospheric Pressure*

Lag. (secs.).	Hydrogen in	
	Air (°C.).	Oxygen (°C.).
0·5	630°	625°
1·0	619°	618°
2·0	605°	606°
5·0	588°	588°
10·0	577°	575°
15·0	572°	—

(*b*) *Ignition Temperatures of Methane at Atmospheric Pressure*

Lag. (secs.)	Methane in	
	Air (°C.).	Oxygen (°C.).
0·5	—	670°
0·6	746°	676°
1·0	728°	657°
2·0	710°	641°
3·0	694°	629°
10·0	657°	602°

Influence of Pressure and Other Factors

It should be borne in mind that the lowest temperature at which inflammation will occur in an explosive medium will also vary with the chemical composition, pressure and velocity of flow (if any).

The influence of pressure may be seen from the following most recent results obtained by H. B. Dixon. For this work his concentric tube furnace was enclosed in a strong steel case (*vide* Fig. 6) which allowed the pressure to be varied either above or below the normal. This enclosing of the furnace also had the further effect of rendering the heating of the silica cylinder more uniform throughout.

TABLE VIII.—INFLUENCE OF PRESSURE ON IGNITION TEMPERATURES (DIXON)

Ignition Temperatures in °C of Hydrogen at Different Pressures

(a) In Air

Lag.	75 mm.	100 mm.	200 mm.	400 mm.	600 mm.	760 mm.	1000 mm.	Atmospheres.			
								2	3	5	7
0·5 sec.	502°	515°	553°	594°	620°	630°	632°	628°	624°	618°	611°
5 secs.	—	—	541°	572°	585°	588°	592°	591°	591°	590°	589°
15 secs.	—	—	—	563°	570°	572°	573°	572°	567°	565°	563°

(b) In Oxygen

Lag.	75 mm.	100 mm.	150 mm.	200 mm.	400 mm.	760 mm.	3 Atms.
0·5 sec.	500°	512°	533°	550°	591°	625°	618°
5 secs.	—	—	—	539°	566°	588°	565°
10 secs.	—	—	—	536°	561°	575°	546°

Ignition Temperatures in °C of Methane at Different Pressures

(a) In Air

Lag.	100 mm.	200 mm.	400 mm.	600 mm.	760 mm.	1520 mm.	Atmospheres.		
							3	5	7
0·6 sec.	815°	788°	765°	753°	746°	722°	705°	675°	653°
5 secs.	—	697°	683°	679°	677°	666°	—	—	—
10 secs.	—	673°	664°	659°	657°	—	—	—	—

(b) In Oxygen

Lag.	75 mm.	100 mm.	200 mm.	400 mm.	600 mm.	760 mm.
0·5 sec.	727°	728°	732°	720°	696°	670°
5 secs.	—	642°	633°	625°	621°	619°
10 secs.	—	633°	621°	611°	604°	602°

Commenting on these results Dixon said : " The effect of variations of pressure on hydrogen and on methane in air is, at first sight, very different. When the air in the cylinder is reduced below the atmospheric pressure the rapid ignition-point of hydrogen falls while that of methane rises. Conversely, when the air in the cylinder is raised above the atmospheric pressure, the rapid ignition point of hydrogen rises while that of methane falls. On further trial it is found that for each gas there is a pressure at which the ignition point is highest, on each side of this crucial pressure the ignition points fall. But whereas the crucial pressure for hydrogen in air is found to be about 1000 mm. of mercury, that of methane is below 100 mm.—in fact too low to be measurable in our apparatus. When methane is introduced into oxygen the crucial pressure is found to be 200 mm.; below this pressure the ignition point falls. All the other gases that have been tested so far in the concentric tube—ethane, ethylene, propylene, acetylene, carbon monoxide and cyanogen—shew the same property with varying pressures."

The influence of velocity of flow of a mixture upon its ignition temperature may be judged from some recent work by Mitscherlich * upon the 'explosion temperatures' of hydrogen-oxygen mixtures. He determined the temperature at which different mixtures of the two gases exploded when flowing, at various velocities and pressures, through an unglazed porcelain tube of 6 mm. internal diameter. He found that whilst the diameter of such a tube, so long as it exceeded 3·6 mm., was *per se* without influence upon the ignition temperature, the pressure and rate of flow of the mixture were material factors, as the following results shew:

TABLE IX.—IGNITION TEMPERATURES FOR ELECTROLYTIC GAS ($2H_2+O_2$) FLOWING THROUGH A HEATED PORCELAIN TUBE (6 MM. INTERNAL DIAMETER) (MITSCHERLICH)

(*a*) *Pressure*—150 *mm.*

Velocity of flow in c.c.'s per minute per cm.^{2} cross-section - - - -	280	187	130	93	37
Observed ignition temperature (°C.) -	592°	592°	593°	594°	601°

(*b*) *Velocity*—37 *c.c. per minute per cm.*^{2} *cross section*

Pressure in mm. - - - - -	150	250	350	450	550	650
Observed ignition temperature (°C.) -	592°	621°	638°	648°	656°	663°

And, as illustrating the observed influence of varying composition of the gaseous medium in his said experiments, the following data are of interest:

TABLE X.—IGNITION TEMPERATURES OF HYDROGEN-OXYGEN MIXTURES (MITSCHERLICH)

Volumetric Composition of Mixture.		Observed Explosion Temperature at:		
H_2	O_2	200 mm. (°C.).	300 mm. (°C.).	400 mm. (°C.).
8	2	593°	611°	620·5°
7	3	587°	605°	615°
6	4	585°	604°	614°
5	5	580°	599°	612°
4	6	575°	594°	607°
3	7	570°	589°	604°
2	8	563°	584°	600°

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* *Zeit. anorg. Chem.* 121 (1921), pp. 55–63.

The ‘ explosion temperature ’ was thus found to be steadily reduced by increasing the oxygen content, as indeed had been shewn previously by H. B. Dixon and J. M. Crofts in their experiments on the ignition of hydrogen-oxygen mixtures by adiabatic compression (*q.v.*), a result which is of considerable theoretical significance.

Relative Ignitabilities of Methane-Air Mixtures

W. Mason and R. V. Wheeler have determined the following ‘ relative ignitabilities ’ of a series of methane-air mixtures at atmospheric pressure, expressed in each case as the lowest temperature to which an enclosure need be heated in order to inflame the mixture when passed into it.[*]

Per cent. methane -	3·0	5·85	7·0	8·0	9·0	10·0	12·0	13·0
Temperature of enclosure required for ignition -	700°	695°	698°	701°	707°	713°	726°	732°

Other results similarly obtained by them for other paraffin hydrocarbon-air mixtures[†] are shewn in the curves included in Fig. 7.

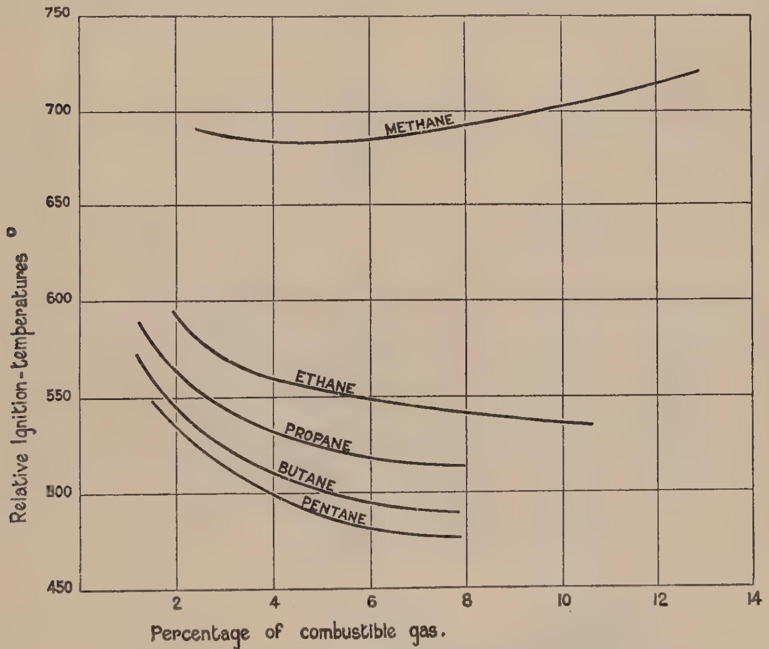

FIG. 7.—RELATIVE IGNITION-TEMPERATURES OF PARAFFIN HYDROCARBON-AIR MIXTURES. (Mason and Wheeler.)

Spontaneous Ignition Temperatures of Some Liquid Fuels

Some interesting experiments upon vapourised liquid fuels were carried out in 1917 by H. Moore, whose object was to obtain data for Diesel engine purposes.* His apparatus consisted of a mild steel cylinder 4 inches in diameter and 3¼ inches deep, the upper part of which was machined to receive a platinum crucible with a screw cover, which served as a combustion chamber. A slow current of air or oxygen preheated to the experimental temperature was passed at a constant rate through the crucible, which was also maintained at the constant experimental temperature. At an appropriate moment a drop of the liquid fuel under examination was allowed to fall, through a hole in the centre of the cover, into the combustion chamber; and, by a process of trial and error, the minimum temperature to which the chamber and air (or oxygen) had to be heated before an explosion resulted some 10 or 12 seconds afterwards, was determined. It was found that agreement to within 3° C. between different experiments with the same liquid was obtainable; some of the results were as follows:

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[*] *Trans. Chem. Soc.* **121** (1922), p. 2079.

[†] *Loc. cit.* **125** (1924), p. 1869.

Table XI.—Ignition Temperatures of Liquid Fuels (Moore)

Liquid Fuel.	Specific Gravity.	Ignition Temperatures (°C.).	
		In Oxygen.	In Air.
Mexican petrol	0·718	279°	361°
Benzol 100 %	0·875	566°	—
Toluol 90 %	0·863	516°	—
Alcohol	0·817	395°	518°
Ethyl ether	0·730	190°	347°

The Instantaneous Ignition of Explosive Mixtures

In 1917 J. W. M'David made some experiments with the object of eliminating, as far as possible, the influence of the time factor (lag), so as to ascertain the minimum temperature to which a given gaseous mixture must be heated, by the sudden application of a hot body so as to cause its instantaneous ignition. The source of heat used was either an electrically heated wire or an iron block, the temperature of which at the moment of ignition could be accurately determined. The results obtained by the method finally adopted were as follows: †

	°C.
Coal-gas–Air	878°
Ethylene–Air	1000°
Hydrogen–Air	747°
Carbonic oxide–Air	931°
Petrol (fraction 0-80°)–Air	995°
Benzene–Air	1062°
Ether–Air	1033°

He concluded definitely that "pure methane when mixed with air does not ignite below 1000°." On the other hand, H. B. Dixon has recently shewn that the minimum ignition point of methane in air is about 650° C., which for 'safety purposes' should always be assumed.

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* *J.S.C.I.* xxxvi. (1917), p. 109.

† *Trans. Chem. Soc.* 111 (1917), pp. 1003–1015.

Ignition by Adiabatic Compression

Falk's Experiments

During the years 1906–1907, H. G. Falk,* acting on a suggestion by W. Nernst, endeavoured to determine the ignition temperatures of various gaseous explosive mixtures by compressing them in a steel cylinder, the piston of which was suddenly driven in by means of a falling weight. With four such machines the following different cylinder dimensions were employed:

Cylinder Dimension.	No 1.	No. 2	No. 3.	No. 4.
Internal length - -	20·82	23·06	25·46	24·124 cm.
Internal diameter - -	2·50	4·40	2·58	5·078 cm.
Thickness of walls - -	0·51	0·73	1·325	1·278 cm.
Internal volume - -	69·80	283·90	101·70	377·50 c.c.

In each experiment the cylinder was filled with the gaseous mixture through a side-tube 5 mm. in diameter, and the subsequent compression was obtained by allowing a known weight to fall on the piston. By increasing the weight and the distance of its fall, the resulting compression of the gaseous mixture could be progressively increased up to the minimum required to ignite it. Falk assumed (i) that the mixture was heated adiabatically and uniformly throughout its whole mass until it reached the ignition point, (ii) that the whole mass then detonated instantaneously, and (iii) that the downward movement of the piston was arrested at the moment of ignition. Accordingly, from the observed minimum compression required for ignition, he calculated the ignition temperature in each case. From his results he concluded that the compression ratio p_2/p_1, and therefore the ignition temperature, is independent both of the initial and final pressures, and nearly so of the cylinder dimensions. Thus for electrolytic gas ($2H_2+O_2$), he obtained the following ignition temperatures in his different machines:

No. 1.	No. 2.	No. 3.
533°	541°	545°

For different mixtures of hydrogen and oxygen (in apparatus No. 2) he obtained:

Mixture.	Calculated Ignition Temperatures (°C.).
$4H_2+O_2$ - - - - - - -	614°
$2H_2+O_2$ - - - - - - -	541°
H_2+O_2 - - - - - - -	518°
H_2+2O_2 - - - - - - -	530°
H_2+4O_2 - - - - - - -	571°

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* *Jour. Amer. Chem. Soc.* 28 (1906), 1517; 29 (1907), 1536; also *Ann. Physik.* (vi.), 24 (1907), p. 450.

From results obtained with apparatus No. 3 he deduced (*inter alia*) the following :

Mixture.	Ignition Temperature (°C.).
$2H_2 + O_2 + N_2$	573°
$2H_2 + O_2 + 4N_2$	649°
$6CO + O_2$	721°
$4CO + O_2$	628°
$2CO + O_2$	601°
$CO + O_2$	624°
$2CO + O_2 + N_2$	634°
$2CO + O_2 + 2N_2$	685°

From the fact that of all the various hydrogen and oxygen mixtures which he examined the equimolecular one required the least degree of compression for ignition in his apparatus, Falk concluded that " hydrogen peroxide must be the first product of the reaction between hydrogen and oxygen."

H. B. Dixon's Experiments

When, however, H. B. Dixon and his co-workers took up the subject in the year 1910 they had no difficulty in shewing, whereas of Falk's aforesaid three assumptions, (i) may in certain cases be practically true, (ii) and (iii) cannot be allowed. Moreover, it was pointed out, that, because he neglected to stop the descent of the piston the moment the gases were brought to the true ignition point in his experiments, his results are unreliable. Indeed, by photographing the explosion produced by the adiabatic compression of such mixtures on a rapidly moving film, Dixon found that, although the flame does start from a point, yet, in the more slowly burning mixtures, it takes an appreciable time to spread throughout the whole of the gas, so that only in the case of fast burning mixtures can the time factor be regarded as negligible. Thus, for example, with undiluted electrolytic gas the photographs shewed that (1) whereas flame always starts from one point, and the explosion wave is very quickly set up, the mass of the gas is not fired instantaneously, and (2) although the time required for the flame to reach the piston is negligible, that required to set up the explosion wave is not negligible. In other words, Dixon concluded that explosive gaseous mixtures do not usually 'detonate' when fired by adiabatic compression, and that the real ignition point usually does not synchronise with the appearance of flame. Hence, it is evident that the pre-flame period is not negligible, and, therefore, that in any determination of ignition temperatures by this method the piston should be stopped at the beginning of the pre-flame period, a precaution which Falk had neglected.*

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* For details of this criticism the reader is referred to H. B. Dixon's Presidential Address to the Chemical Society, 1910 (*Trans. Chem. Soc.* **97**, pp. 674–677) ; also to H. B. Dixon, L. Bradshaw and C. Campbell, *Trans. Chem. Soc.* **105** (1914), p. 2027.

In 1914 H. B. Dixon and J. M. Crofts published the results of their repetition of Falk's experiments, using an improved apparatus (Fig. 8), in which the precautions referred to had been observed. They calculated the ignition temperatures from the observed compressions, by means of the formula:

$$\frac{T_2}{T_1}=\left[\frac{V_1}{V_2}\right]^{\gamma-1},$$

where T_1 and T_2=the initial and final temperatures (on the absolute scale), and V_1 and V_2 the initial and final volumes of the gaseous mixture, whilst γ=the ratio of its specific heat at constant pressure to that at constant volume (assumed to be 1·4 for the diatomic gases hydrogen, oxygen and nitrogen). They also assumed the compression of the mixture in the cylinder to have been adiabatic in all cases, whilst recognising that this was not strictly true. Such error is indeed inherent in the method, and, although probably very small, at present there is no means of allowing for it.

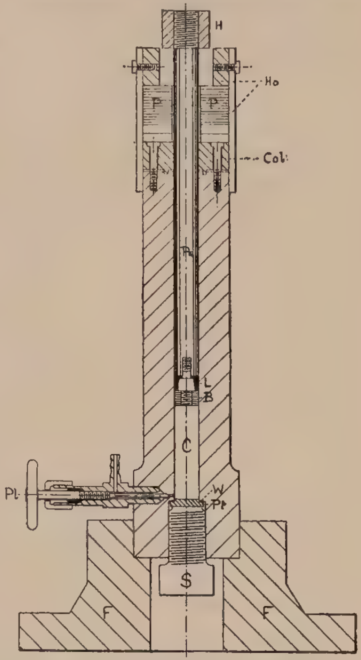

FIG. 8.—DIXON AND CROFTS' APPARATUS.

The ignition temperatures so calculated from their observed minimum 'compression ratios' required for ignition, shewed that, whereas successive additions of hydrogen or nitrogen to electrolytic gas progressively raise its ignition temperature by regular increments in each case, successive additions of oxygen lower it, as follows:

TABLE XII.—THE IGNITION TEMPERATURES ON ADIABATIC COMPRESSION OF DILUTED ELECTROLYTIC GAS MIXTURES (DIXON AND CROFTS)

Electrolytic Gas, $2H_2+O_2$=526° C.					
$+xH_2$.	°C.	$+xN_2$	°C.	$+xO_2$	°C.
$x=1$	544°	$x=1$	537°	$x=1$	511°
$x=2$	561°	$x=2$	549°	$x=7$	478°
$x=4$	602°	$x=4$	571°	$x=14$	472°
$x=8$	676°	$x=8$	615°	—	
$(526+18x)°$		$(526+11x)°$		—	

These results are plotted in the curves shewn in Fig. 9.

The observed raising effects of successive dilutions with hydrogen call for no particular comment, save that the greater effect of hydrogen, as compared with nitrogen, is probably due to its greater thermal conductivity. The lowering effect of excess oxygen, which did not stop at the equimolecular ratio, is indeed puzzling, and its meaning can only be conjectured. Dixon and Crofts suggested at the time that it may be due to the formation of some active polymeride of oxygen under the experimental conditions. Such a supposition, however, seems to us doubtful. It may be that ignition is not altogether a purely thermal phenomenon, a question which will be further discussed in our next chapter.

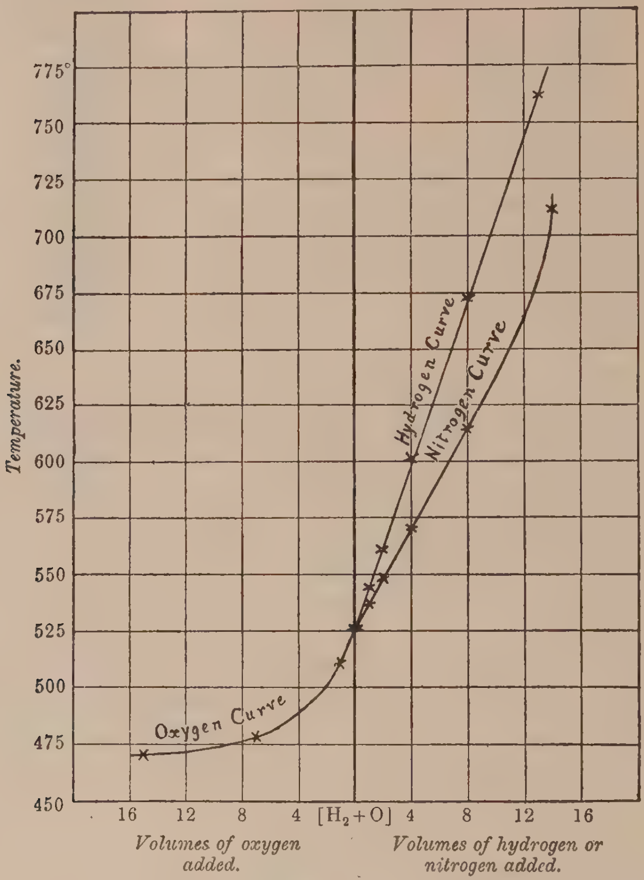

FIG. 9.

Dixon has recently improved his compression apparatus, as the result of a suggestion by Tizard and Pye, who pointed out that if the piston is only arrested, and not held in place, when the ignition-compression is reached, the gas during the self-heating pre-flame period may do work against the piston and so be cooled, a source of error particularly affecting slow-firing mixtures. Accordingly Dixon devised an arrangement whereby the piston was firmly held on the ignition compression being reached. Moreover, in his latest apparatus, of larger capacity than the first, a Ricardo toggle-joint has been employed.

The revised figures are as follows :

TABLE XIII.—IGNITION TEMPERATURE ON ADIABATIC COMPRESSION. RECENT DETERMINATIONS (DIXON)

Mixture.	Old Machine. Piston free.	Old Machine. Piston Clamped.	New Machine. Piston held.
$2H_2+O_2$	526°	523°	521°
$2H_2+2O_2$	511°	507°	501°
$2H_2+8O_2$	478°	472°	458°
$2H_2+16O_2$	—	462°	438°
CH_4+3O_2	366°	341°	340°
CH_4+5O_2	382°	347°	345°
CH_4+15O_2	420°	387°	377°

Tizard and Pye's Experiments

In 1922 H. T. Tizard and D. R. Pye, in publishing the results of experiments upon hydrocarbon-air mixtures,* remarked that, although in experiments with such mixtures as diluted electrolytic gas, where the time interval between the end of the compression and the occurrence of ignition is very small, the apparatus used by H. B. Dixon and J. M. Crofts would probably give fairly satisfactory results, it is not so well suited for experiments with other gases, such as hydrocarbons, where there may be an appreciable delay before ignition occurs. They also pointed out that the 'ignition temperature' of a given explosive mixture cannot be a really definite property, but must vary according to experimental conditions; and that for any particular condition it must be "that temperature at which heat is being evolved by the reaction at a slightly greater rate than that at which it is being dissipated externally." Moreover, they consider Dixon's calculations open to criticism on the ground that the actual temperature of the gaseous medium after sudden compression can hardly be (as he assumed) uniform throughout, although there may be no information available as to the temperature gradients which may exist under such conditions.

In their own experiments, which aimed at determining the temperature of spontaneous ignition of mixtures of various vapourised fuels with air in internal combustion engines, under conditions corresponding with those obtaining in practice, Tizard and Pye used an apparatus consisting essentially of a water-jacketed cylinder (internal diameter = 4 inches) with a piston (stroke = 8 inches), whose motion was actuated by a very heavy fly-wheel kept spinning by an electric motor at about 350 r.p.m. The initial temperature of the gases in the cylinder could be varied by means of the water-jacket, and the variation of pressure during and after compression was recorded by means of an optical pressure indicator of the Hopkinson type. A timing device also measured the interval between compression and explosion. Equations were developed for deducing the relation between rate of cooling and velocity of reaction at different temperatures; from such equations the theoretical delays were calculated and found to be in good agreement with the experimental values.

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* *Phil. Mag.* **44** (1922), p. 791.

In some experiments a fan was kept running in the cylinder to increase the rate of heat loss up to about three times. An experiment consisted in first finding the lowest ignition temperature for a given mixture, *i.e.* where the rate of heat evolution just exceeds that of its dissipation, and then determining the coefficient of the reaction velocity; the times taken for the reaction to reach completion at any given temperature were also calculated and compared with the observed lags between the moment of maximum compression and the subsequent explosion of the gas mixture in each given experiment. As an example, the following results for a mixture of 1 part by weight of heptane with 20 parts by weight of air may be quoted:

TABLE XIV.—IGNITION OF 1 TO 20 (BY WEIGHT) HEPTANE–AIR MIXTURE (TIZARD AND PYE)

(i) Fan not used.		(ii) Fan running at Full Speed.	
Temp. (°C.).	Lag. (sec.).	Temp. (°C.).	Lag. (sec.).
282°	0·51	309°	0·20
296·5°	0·164	319°	0·13
319°	0·063	348°	0·027
429°	0·003	371°	0·013

Therefore, according to the authors referred to, the heptane-air mixture would eventually ignite (after 0·51 sec.) if its average temperature were raised by compression to about 280° C., although in such circumstances probably the portion of it which actually ignites is at the true ‘adiabatic ignition temperature,’ which they consider to be about 319° C.

In a later paper Tizard and Pye* described an improved form of their apparatus (illustrated in Fig. 10), in which the gaseous mixture could be heated initially to any desired temperature up to 180° C. before compression by means of an oil-jacket round the working cylinder, whose diameter was three inches, with an eight-inch piston stroke. Owing to the inertia of the working parts it took a constant 0·14 sec. for compression. From the experimental observations it was concluded that ignition occurs

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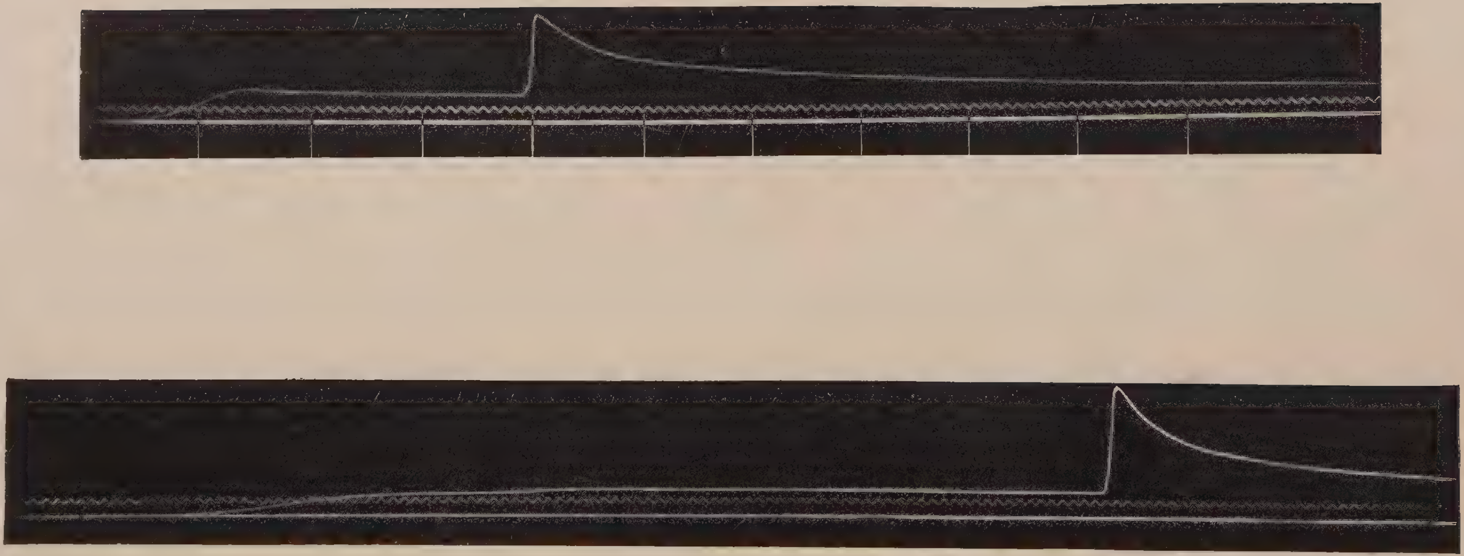
* *Phil. Mag.* (7), **1** (1926), p. 1094.

PLATE I.



Typical Pressure-time Records shewing Ignition of Gaseous Explosive Mixtures on Adiabatic Compression. (Tizard and Pye.)
(From the *Philosophical Magazine.*)

very locally, and that no criterion of the temperature at such locus or loci can be inferred from the mean pressure of the explosive mixture as recorded by the indicator. It was found that, "though in some cases the compression pressure remains constant or rises slightly during the delay period . . . in the majority of cases at or near the minimum ignition temperature there is a fall of pressure during the delay period, and this fall can occur at a rate which is practically the same as the rate of fall of pressure when no ignition occurs." This effect is shewn in the two typical pressure-time records reproduced in Plate I. It was, however, considered that such circumstances could not upset the conclusions drawn, or the calculations made in their previous paper, because the rate at which the nucleus of combustion is losing heat probably bears some relation to the average rate for the whole gas.

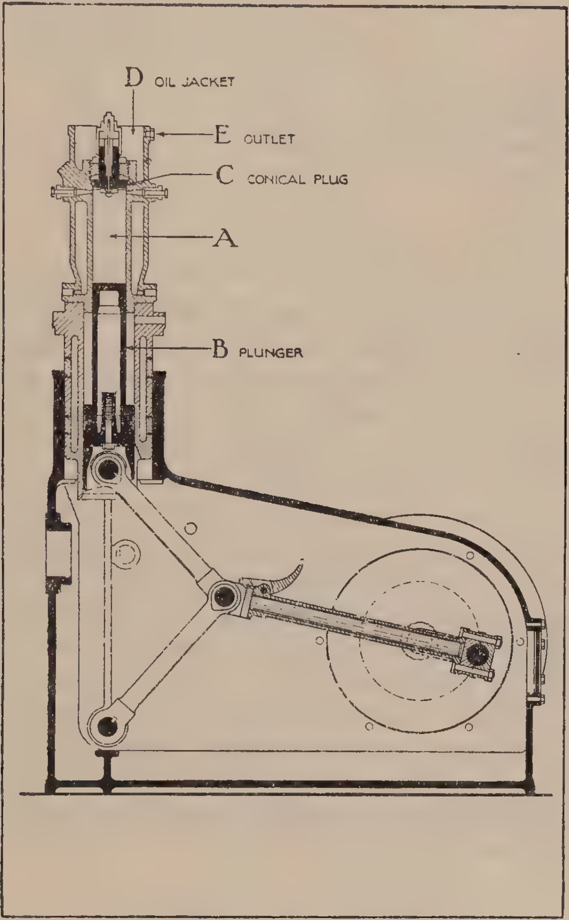


FIG. 10.—TIZARD AND PYE'S APPARATUS.
(From the *Philosophical Magazine.*)

The following summarised results with the new machine were given :

TABLE XV.—IGNITION TEMPERATURES ON ADIABATIC COMPRESSION (TIZARD AND PYE)

Mixture.	Initial Temperature.	Minimum ‘ average ’ Temperature of Compression to produce Ignition.
Pentane–Air -	91·5°	316°
Hexane–Air -	78°	307°
Heptane–Air -	66°	298°
Octane–Air -	60·5°	297°

Concluding Remarks

It will be clear, from what has been set forth in this chapter, that the ignition of a gaseous explosive mixture, so far from being so simple a matter as was formerly supposed, involves many different factors. Therefore, it is hardly possible to give any rigid definition of what is usually termed its ‘ignition temperature,’ which indeed is no definite physical constant. It can, however, be said that it is now possible to determine experimentally with a fair degree of precision, by methods evolved during the present century, the lowest temperature at which a given mixture will ignite in given circumstances, and to shew the influence of such factors as pressure upon it ; but in every case the ‘ time-factor ’ (‘ lag ’) is of great, and often paramount, importance. There also remains the question, about which we are still very much in the dark, whether ignition can be regarded rightly as a thermal (*i.e.* temperature) process only, and to what extent (if any) ‘ ionisation ’ is involved in it. For, in default of a complete understanding of ignition phenomena, our theories of flame propagation through gaseous explosive media must remain, to some extent at least, provisional.

CHAPTER IX

THE IGNITION OF EXPLOSIVE MIXTURES BY ELECTRIC DISCHARGES

THE practice of igniting explosive mixtures by electric discharges is so common nowadays that it is surprising how little the phenomena associated with it have been investigated up to the present. Indeed, upon the important question as to whether, or how far, the igniting power of a given spark is due primarily to its temperature or to its ionising effect there is still much difference of opinion among competent observers, shewing that the subject is still very obscure. In this chapter, therefore, no more will be attempted than to acquaint the reader with the principal facts at present known concerning it.

We owe the first systematic researches upon the subject to W. M. Thornton, whose results were published during the years 1914–1916.* He pointed out that, whereas at that time it was being assumed generally that the processes of ignition and flame propagation are thermal throughout, recent work on the ionisation of gases had shewn that a molecule can be ionised by corpuscular radiations, and that by the gain or loss of such corpuscles its ‘activity’ can be profoundly modified. Hence, it had become necessary to consider whether, and if so how far and in what sense, ‘ionisation’ is a necessary precedent to combustion, and to examine experimentally the mechanism of electrical ignition.

Finch and Cowen's Researches

Before dealing with Thornton's results in detail, however, it seems desirable to refer to the more recent work of G. I. Finch and L. G. Cowen † at the Imperial College of Science and Technology, London, upon ‘the Combustion of Electrolytic Gas in Direct Current Discharges,’ because it has brought to light several new and important fundamental points in connection with the slow (non-explosive) combination of the gases in such discharges at various pressures between 30 and 90 mm. Some years previously Kirkby* had studied the effect of steady direct-current discharges on electrolytic gas at pressures below those at which ignition can occur, finding that (provided the circumstances of the discharge, including pressure, current and degree of separation of the electrodes were constant) the amount of water formed is proportional to the quantity of electricity passed in the discharge, and independent of the nature of the electrodes, and that " the chemical action took place at all points of the discharge." Finch and Cowen have taken the matter very much further, demonstrating in a very beautiful and conclusive manner conditions under which the combustion is primarily determined by the ionisation of the gaseous medium through which the current passes, and not by either temperature or other thermal factors, wherein lies the significance of their work.

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* *Proc. Roy. Soc.* A. **90** (1914), pp. 272–297; **91** (1914), pp. 17–22; **92** (1915), pp. 9–22; and pp. 381–401.

† *Proc. Roy. Soc.* A. **111** (1926), pp. 257–280.

In the experiments a perfectly steady direct-current discharge was maintained between suitable electrodes of platinum or copper in pure electrolytic gas, confined over pure sulphuric acid, at pressures between 30 and 90 mm. in such a manner as to eliminate, as far as possible, any chemical combination, including that due to heat, other than that caused by the ionisation of the gases. The proportionality between the rate of chemical change and the current was then carefully studied. For further details the original paper must be referred to. It was shewn that :

(i) an electric discharge can be passed through electrolytic gas in such a manner that combination takes place at a rate which is determined only by the discharge ;

(ii) up to a certain limiting current, which depends upon (*a*) the nature of the cathode, (*b*) the gas pressure, and (*c*) the degree of separation of the electrodes, combustion is confined to the cathode zone ;

(iii) such cathode combustion is independent of (*a*) the potential fall between, and the degree of separation of the electrodes, (*b*) the gas pressure, and (*c*) the temperature of the discharge, but depends on the nature of the cathodic material, its rate being somewhat greater with platinum than with copper electrodes ;

(iv) the rate of such cathodic combustion is directly proportional to the current, *i.e.* to the number of ions arriving at the cathode in a given time ;

(v) after a certain limiting current has been exceeded, combustion commences abruptly in the inter-electrode zone (which is strongly suggestive of a quantum effect), and is thereafter superposed upon the aforesaid cathodic combustion, the two then continuing as independent simultaneous effects ;

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* *Proc. Roy. Soc.* 85 (1911), pp. 151 to 174.

(vi) the said inter-electrode combustion is itself, like the cathodic, also proportional to the current passing; unlike the cathodic, however, it is independent of the material of the electrodes, but dependent upon (*a*) the gas pressure, and (*b*) the degree of separation of the electrodes;

(vii) little or no combustion takes place in the anode zone.

Such being the facts disclosed by these experiments, it seems difficult to resist the conclusion that the non-explosive combustion which had taken place in both the cathode and inter-electrode zones was primarily determined by the ionisation of the gaseous medium through which the current passed, and was independent of purely thermal factors. In the case of the cathodic combustion its rate was independent of pressure. At all events a non-explosive combustion has thus been demonstrated under conditions such that it is primarily due to electrical and not to thermal conditions.

Another important feature of the experiments, which particularly bears upon the subject of this chapter, was that, in certain cases after a definite current had been exceeded, the c/i ratios (where c=rate of combustion, and i=current passing), which up to then had all fallen on inclined straight lines, suddenly and very rapidly increased, so as to fall on almost vertical lines, until the gases ignited and an explosion ensued. Photographs subsequently taken shewed that ignition had invariably occurred at a point near the anode, *i.e.* at the root of the positive column, presumably where the greatest concentration of ions exists in the discharge. These circumstances led Finch and Cowen to put forward the following suggestive view of the mechanism of electrical ignition of explosive gaseous media:

"When an electric discharge, powerful enough to bring about ignition, is passed through such a medium, chemical combination occurs in both the cathode and inter-electrode zones. The rate of such combustion is directly proportional to the current; that in the cathode zone being proportional to the total number of ions arriving in unit time at the cathode, and that occurring in the inter-electrode zone (positive column) being probably proportional to the number of suitable ions formed by the passage of the current. The heat liberated by the gases on combination contributes to the number of ions formed by the passage of the current. With an igniting current this heat source of ionisation produces ions more rapidly than they recombine to electrically neutral atoms or molecules, or are removed from the zone of the discharge by convection currents in the gas. Thus the source of ionisation is cumulative and leads to ignition and explosion when a sufficient concentration of suitable ions has been attained. Furthermore, ignition does not occur at the actual moment of initial passage of the igniting current, but only after the lapse of a definite time interval, or lag, during which that cumulation of suitable ions which is necessary to bring about ignition is gradually attained by the cumulative addition of these ions which are formed by the heat of combination of the combustible gases to the ions due to the passage of the current."

Whatever may be the final verdict upon the view thus tentatively advanced by the authors in question, it undoubtedly focuses attention upon some cardinal points, and affords a possible explanation of the curious 'lags' observed by Dixon and others in their experiments on the thermal ignition of explosive gaseous media. It also helps us to visualise the inter-relation of the thermal and 'ionisation' factors in ignition.

W. M. Thornton's Experiments

Thornton shewed that for given sparking conditions (*e.g.* electrodes, type of discharge, voltage, etc.) a certain 'minimum igniting current' is required to ignite a given explosive mixture under given conditions. Both direct and alternating currents were used. He argued that, if ignition was purely a thermal process, the igniting power of a spark in any given case should be proportional to the square of the current in circuit; on the other hand, if it were primarily ionic, it would be proportional to the current, when this is unidirectional, but different for unidirectional and alternating currents of equal strengths. And, taken as a whole, his experimental results seem to support the latter view.

In most of his experiments Thornton used a cylindrical glass explosion vessel $2\frac{1}{4}$ inches in diameter and 5 inches long, with ends joined to $\frac{3}{8}$-inch tubes, and having two transverse arms $\frac{5}{8}$-inch in diameter, fitted with corks through which the electrodes (one fixed and the other moveable) passed. These were of iron, copper or nickel, bent to cross at right angles, giving a point contact which could be renewed by sliding the moveable pole away, and making contact on the other side of the fixed one. The break was made by rotating the moveable pole through a right angle.

G. I. Finch has pointed out * that, inasmuch as the discharge was produced by opening a circuit in which a known current (direct or alternating) was flowing, the rate of dissipation of energy in it could not be constant; it would attain a maximum at or shortly after the opening of the circuit and would thereafter fall as the gap widened, ultimately becoming zero with extinction of the discharge. And, therefore, although the current flowing prior to opening the circuit might be known, in the case of direct current it could not be assumed to be equal to the maximum that passed in the discharge itself. With alternating currents additional complications would arise, in that the value of the maximum current would also depend upon the phase angle and frequency of the supply, as well as upon the actual moment at which the opening of the circuit began. In this connection J. D. Morgan and R. V. Wheeler have studied ignition by high tension discharges produced by means of an induction coil or magneto across a fixed gap.* Taylor-Jones has examined in detail the extremely complex nature of this type of discharge, which is 'oscillatory,' a single discharge consisting of a train of sparks.† Morgan,‡ as well as Patterson and Campbell,§ have shown that the igniting power depends solely in the energy associated with the first oscillation, and not in the total energy dissipated in the complete train of oscillations of a single discharge. The rate of dissipation of energy is not constant, and the maximum and mean currents thereof are difficult to ascertain without a suitable oscillograph.

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* *Loc. cit.* p. 259.

Another circumstance which must not be forgotten is that the region of a discharge, particularly when passing in a gas under normal pressure, is a zone of high temperature, and contains the vapour of the electrode material; also in oscillating discharges, intense pressure waves are set up in the surrounding gas. Thornton shewed that the nature and condition of the electrode material had a considerable, and sometimes erratic, influence upon the experimental results obtained with his 'break-sparks.' It is, therefore, difficult to compare and interpret much of the published experimental work, because of the fact that the types of electric discharges used by different investigators have involved the introduction of unknown factors (both electrical and otherwise) which have obscured the issues, and the subject needs a thorough *de novo* re-investigation.

As examples of Thornton's results the following curves from his first paper (*loc. cit.*) are reproduced, namely:

Figs. 11 and 12, shewing the least igniting currents found for mixtures of hydrogen and carbonic oxide with air. Continuous current at 100 volts; alternating at 200 volts; frequency = 36; with iron poles.

Fig. 13, shewing the least igniting currents found for paraffin hydrocarbon-air mixtures. Continuous current break-sparks at 100 volts; iron poles.

Attention is directed to the type of curve obtained for hydrogen-air mixtures (Fig. 11) with continuous current break-sparks; it was regarded by Thornton as being the most fundamental of all, because, "in its complete form, with sharp corners and steep sides, it is independent of any chemical combination. . . . It depends only on the electric strength of the mixture or on the ionising power of the break-sparks." In each of the curves in Fig. 13 for the paraffin hydrocarbon-air mixtures there are three distinct portions, the middle one being a straight line passing through, or nearly through, zero, which Thornton regarded as "expressing the fact that over the greater part of the range of inflammability the least igniting current is nearly proportional to the number of molecules of combustible gas in unit volume of the mixture." From this he concluded that ignition was primarily due to the ionisation of the hydrocarbon molecule. Moreover, since the ratio I/P, where I=igniting current and P=percentage of combustible gas in the mixture, was found to be nearly proportional to the number of hydrogen atoms in the molecule, and as hydrogen is the most easily ionised of all gaseous molecules, he regarded it as "at least conceivable that if the effect is due to ionisation, the ignition of the complete molecule of combustible gas is started by ionisation of its hydrogen atoms," a conclusion which, it may be remarked, accords with the generally accepted 'hydroxylation theory' of hydrocarbon combustion (see Chapters XXIX and XXX). In this connection it may be noted, in passing, how Thornton found that the ignition of mixtures with air of an equimolecular methane-hydrogen mixture followed that of methane-air mixtures, which he regarded as "a striking confirmation of Bone's measurements of the relative affinities of methane and hydrogen," shewing that they hold in the very earliest stage of explosion.

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* *Trans. Chem. Soc.* **119** (1921), p. 239.

† *Theory of the Induction Coil* (1921).

‡ *Principles of Electric Spark Ignition.*

§ *Proc. Phys. Soc.* (1919), p. 177.

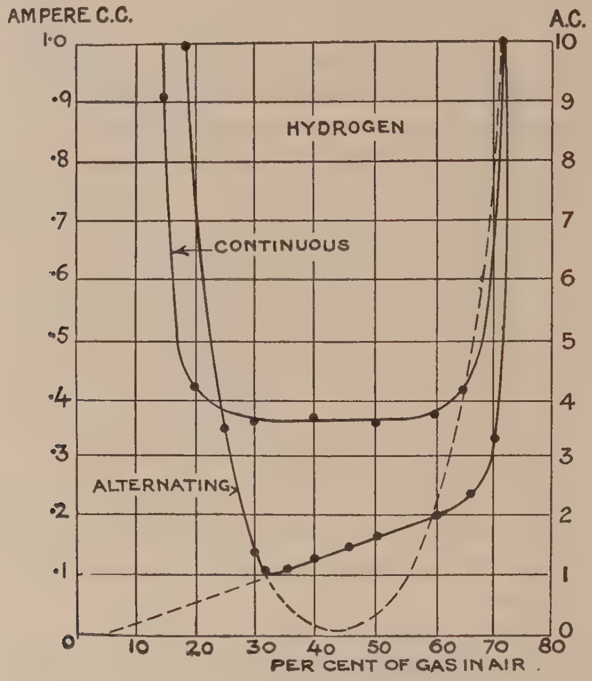

FIG. 11.—LEAST IGNITING CURRENTS OF HYDROGEN-AIR MIXTURES. (Thornton.)

Perhaps it may be thought that Thornton was on less sure ground in his experiments upon ignition by means of condenser discharge and induction sparks, when he observed abrupt increases in the minimum

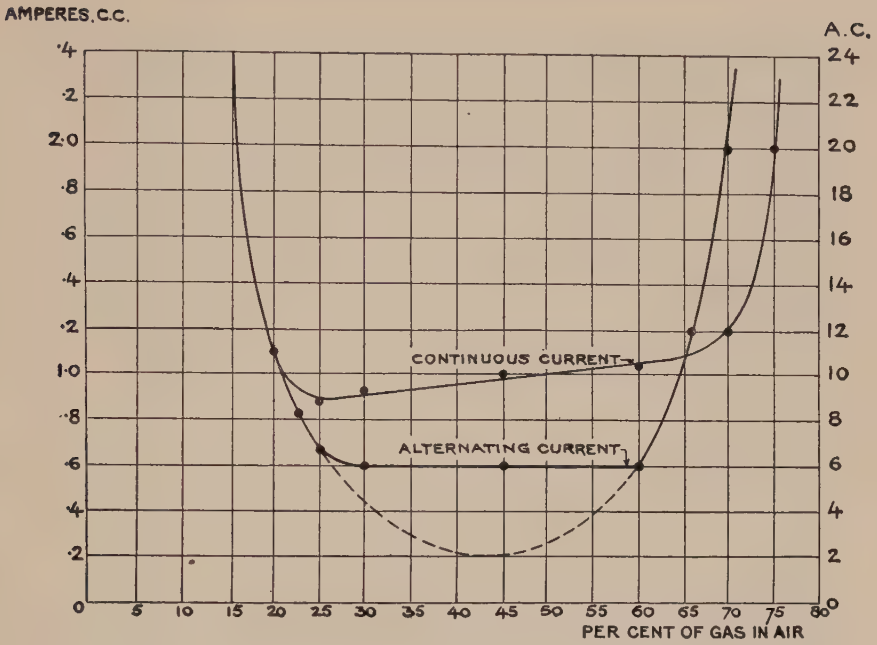

Fig. 12.—Least Igniting Currents of Carbonic Oxide-Air Mixtures. (Thornton.)

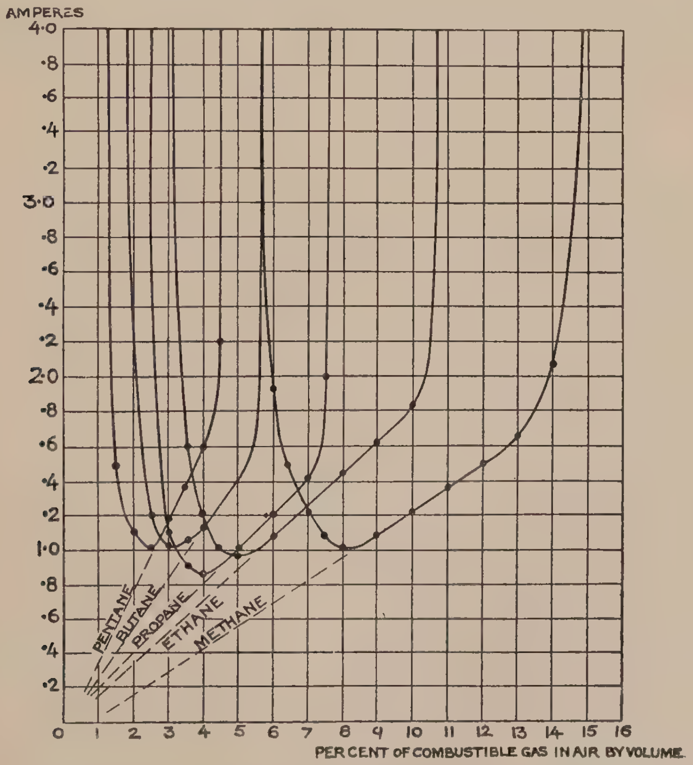

Fig. 13.—Least Igniting Currents of Paraffin Hydrocarbon-Air Mixtures. (Thornton).

igniting current as the proportion of combustible gas in the mixture progressively increased, and for which he claimed to have established what he termed ‘stepped ignition.’ It is, however, difficult to give his results any chemical interpretation, and, although subsequently Paterson and Campbell observed certain irregularities in such cases which led them to suppose that “the igniting power of a spark is very much more sensitive to changes in composition than to the capacity discharging in the spark,” R. V. Wheeler * definitely failed to confirm Thornton’s observations of ‘stepped ignition’ by means of impulsive discharges in the case of methane-air mixtures. And, seeing that Thornton had himself recognised that “with this kind of ignition methane appears to be sensitive to slight changes on the surface of the poles . . . (and) . . . if the poles were not cleaned after every few explosions, steps appeared in the curve even with this gas, which disappeared again when the poles were cleaned,” the jury will perhaps, on the evidence so far submitted, prudently return the verdict of ‘non-proven’ as regards the supposed ‘stepped ignition,’ without necessarily dismissing Thornton’s main conclusions, namely, that it appears probable “from the great difference in magnitude and type between continuous and alternating current that some kind of ionisation precedes combustion, for the evidence is strong that a relation between electrification and chemical change not unlike that of ordinary ionisation occurs at ignition, caused possibly by the violent collisions which must occur in the gas in contact with high-temperature sparks.”

Ignition of Hydrocarbon-Air Mixtures

R. V. Wheeler has investigated more particularly the ‘least igniting currents’ for hydrocarbon-air mixtures by means of impulsive discharges from induction coils,† and Fig. 14 shews his curves in which hydrocarbon percentages over a wide range are plotted against ‘relative igniting currents,’ *i.e.* the currents in the primary circuit of an induction coil which, when broken at a constant rate, induced secondary discharges, at a fixed spark gap, just capable of igniting the mixtures. Unfortunately, the use of an induction coil in such experiments introduced several unknown factors affecting the nature of the discharge, so that the results obtained should be considered as relative and empirical only, and as having significance in relation to the particular experimental conditions only. Albeit, there seems to be sufficient evidence to warrant the belief that in some respects the characteristics of such curves are invariable, namely (*a*) in regard to the greatly increased difficulty of ignition as the limits of inflammability are approached, and (*b*) to the optimum position of ignition, *e.g.*, between 8·2 and 8·5 per cent. methane. Moreover, the results of such experiments have had an important bearing upon the safety of coal-mines, inasmuch as they have enabled estimation to be made as to the maximum voltage permissible in the primary bell-signalling circuits in mines. According to Regulation 134 (*a*) of the 10th July, 1913, this is now 25 volts, it having been proved that when in circuit with any means of supply of electric current up to such voltage, bare-wire connections can be short-circuited and separated in an 8 to 8·5 per cent. methane-air mixture without causing its ignition.

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* *Trans. Chem. Soc.* 117 (1920), pp. 903–913.

† *Loc. cit.* 125 (1924), p. 1860.

J. D. Morgan has considered the important question whether or no in the said spark ignition of explosive mixtures the incendivity of a spark depends upon its total energy, but arrived at a negative conclusion.* For, he argued that, (*a*) it has been proved that, with a low tension spark, the least spark energy required to ignite a given gas mixture diminishes with increase of voltage impressed on the circuit prior to the production of the spark, (*b*) with a high-tension spark (which consists of a capacity component preceding an inductance component) the incendivity of the spark can be increased by increasing the proportion of energy in the initial part of the spark without increasing its total energy, and (*c*) the incendivity of a condenser or capacity spark is greater than an inductance spark dissipating

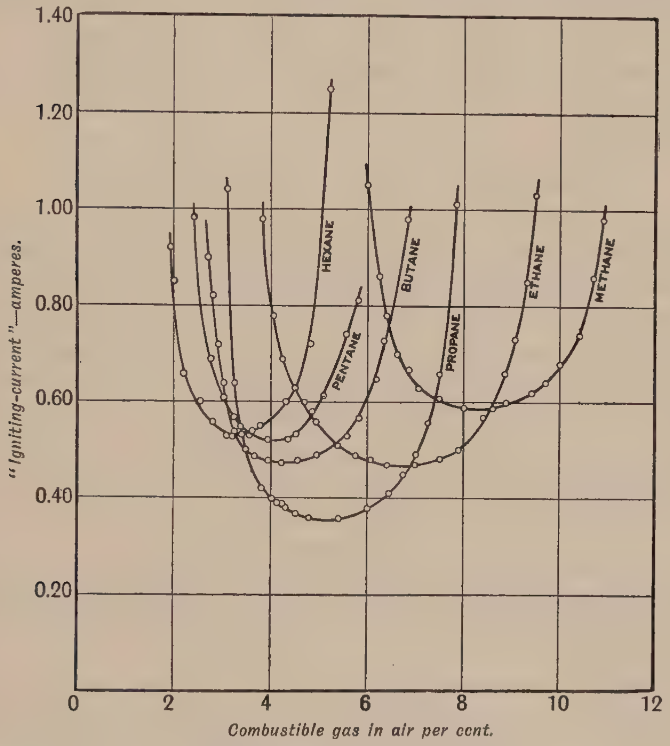

Fig. 14.—Least Igniting Currents of Paraffin Hydrocarbon-Air Mixtures. (Wheeler.)

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* *Trans. Chem. Soc.* **115 (1919), pp. 94–104.**

the same amount of energy. This, he went on to say, "suggests that ignition is due only to the initial part of the spark, and that in every spark there is a certain amount of unused energy which makes no contribution to the process of ignition." This proportion of unused energy, he thought, must diminish as the initial intensity increases, but at present any measurements of the effective portion of the spark appear to be impossible, which would go far to explain the diverse results hitherto obtained by different investigators. From the results of his own experiments, where the minimum igniting sparks under different electrical conditions for a given gaseous explosive mixture had one property in common namely that they all liberated the same amount of heat energy, he inferred, in contradiction with Thornton, that electrical ignition is primarily a thermal phenomenon, at least within certain limits; a conclusion which may not find general acceptance.

The Ignition of Carbonic Oxide-Oxygen Mixtures

The recent work of W. A. Bone and F. R. Weston * has shewn that the progressive removal of water vapour from a mixture of carbonic oxide and oxygen in their combining proportions ($2CO + O_2$) greatly increases the minimum condenser-spark energy required to ignite it; for it was found to be some thirty times greater in the case of a calcium chloride-dried mixture than for one saturated with water-vapour at 17° C. As this is, however, bound up with the question of the mechanism of the combustion of carbonic oxide, its further discussion is reserved until a later chapter. For present purposes it will suffice merely to reproduce the experimental results, which were as follows:

TABLE XVI.—INFLUENCE OF THE AMOUNT OF WATER VAPOUR PRESENT ON THE MINIMUM IGNITING SPARK ENERGY FOR A $2CO + O_2$ MIXTURE (BONE AND WESTON)

Hygroscopic Condition of $2CO + O_2$ Mixture.			Minimum Igniting Capacity of Condenser at 110 volts in microfarads.	Energy of Minimum Igniting Spark. Joules × 10^6.
	Saturation with H_2O at °C.	Per cent. H_2O by Volume Present.		
Mixture 'saturated' at room temperature	17·4	2·00	0·76	4,600
	17·0	1·98		
	14·5	1·70	0·83	5,020
	14·0	1·60	0·98	5,930
Mixtures 'saturated' at a low temperature controlled by ice in some freezing mixture	4·0	0·80	4·00	24,200
	0·0	0·60	4·80	29,040
	−5·0	0·40	8·00	48,400
	−10·0	0·26	10·07	60,900
	−16·0	0·16	17·25	104,350
	−25·0	0·06	18·79	113,800
Mixture $CaCl_2$-dried	- -	0·03	20·83	126,000

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* *Proc. Roy. Soc.* A. 110 (1926), pp. 620–623.

Limiting Ignition Pressures

It should also be mentioned that in 1914 H. F. Coward and his co-workers published * the results of experiments in which the sensitiveness to electric spark ignition of various gaseous mixtures was compared by determining the 'limiting pressures' at which they could be ignited with a given sparking arrangement. It should be noted, however, that the results apply to the particular experimental conditions employed, and not necessarily to any other. The following results were obtained for a series of mixtures of carefully purified gases in the same apparatus:

Mixture.	Minimum Ignition Pressure mm.
$2H_2 + O_2$	81
$2CO + O_2$ (moist)	128
$CH_4 + 2O_2$	120
$C_2H_6 + 3\frac{1}{2}O_2$	75
$C_2H_4 + 3O_2$	65

The effects of dilution were also studied, it being found that either electrolytic gas or a moist $2CO + O_2$ mixture at a pressure somewhat below its minimum ignition pressure may be rendered inflammable by the addition of either oxygen or the combustible gas, or even by moderate dilution with either nitrogen or argon. For particulars, however, the original paper must be consulted. The authors in question, whilst suspecting an 'activation of oxygen' in the ignition of carbon monoxide-oxygen mixtures, concluded that their results "do not indicate whether ignition is ultimately a thermal or an electronic effect, or, if electronic, whether ignition is the result of the high degree of compression in the path of the discharge, due to the mutual repulsion of electrons."

In this chapter an endeavour has been made to present an impartial statement of the principal facts and views which have been discovered or expressed in connection with the experimental investigation of this important subject. On general grounds there is much to be said for the view, which several investigators have adopted, that 'ionisation' is a necessary precedent to combustion, and therefore that the primary function of the spark is an ionising one. On the other hand, the view that electrical ignition is primarily a thermal process is still widely held. Possibly, however, these apparently opposite opinions are not irreconcilable, because ionisation is promoted by temperature, and we know that an electric spark is certainly a region of both intense ionisation and high temperatures, besides other conditions. And there is need for much further experimental investigation, under more rigidly controlled conditions than heretofore, before any final judgment can be passed.

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* *Trans. Chem. Soc.* 105 (1914), pp. 1069–1093.

CHAPTER X

THE LIMITS OF SELF-PROPAGATION OF FLAME THROUGH A GASEOUS EXPLOSIVE MEDIUM

'Flame Caps'

When a flame is introduced into a mixture of inflammable gas and air containing somewhat less of the combustible than suffices to make it explosive, a 'cap' or aureole is formed round the flame; and as the proportion of combustible increases, the cap enlarges. The coal-miner regularly uses this cap formation as a means of detecting, and approximately estimating fire-damp in the atmosphere of mines. Several investigators, among whom may be mentioned F. H. Clowes,* G. R. Thomson,† E. B. Whalley and W. M. Tweedie,‡ and T. Gray,§ have worked on this practical aspect of the subject. It has been observed that when a current of such gas and air mixture passes through a lamp flame, the cap may become detached from the flame and be carried away from it for a limited distance before being extinguished.

A good illustration of such 'cap-formation' over an oil-lamp flame burning in an atmosphere containing less combustible gas than would render it explosive is reproduced (Plate II) from a paper by Messrs. Whalley and Tweedie, in which are described tests made in a Clowes chamber with an oil-lamp for the purpose of comparing the caps formed in atmospheres containing known small percentages of Leeds coal-gas and methane, respectively. The following data shew the relationship between cap-dimensions and percentages of combustible gas in the surrounding atmosphere when using a standard flame 0·07 to 0·10 inches in height.

Table XVII.—Flame-Cap Heights in Atmospheres Containing Varying Proportions of Combustible Gas (Whalley and Tweedie)

Percentage of Combustible Gas in Atmosphere.	Height of Caps in Inches.	
	Coal Gas.	Methane.
0·5	0·25	0·20
1·0	0·27	0·22
2·0	0·40	0·32
2.5	0·45	0·47
3·0	0·55	0·55

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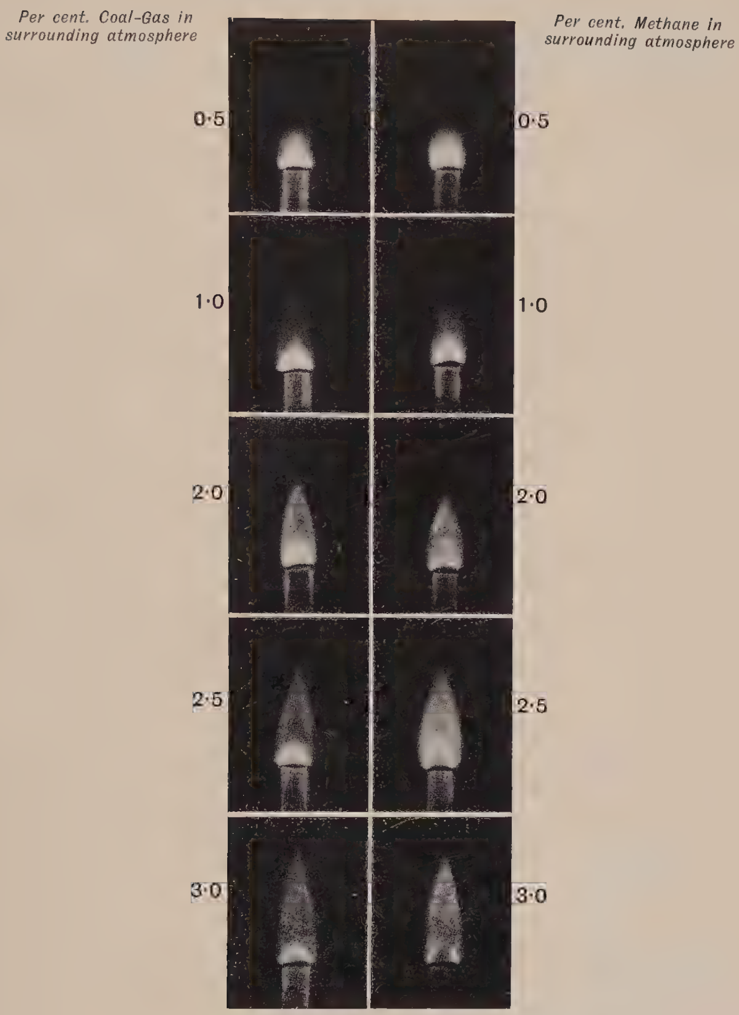
* *Detection and Estimation of Inflammable Gas and Vapour in the Air* (Lockwood, 1896).

† *Trans. Inst. Mining Engr.* 28 (1909), p. 524. ‡ *Ibid.* p. 509. § *Ibid.* p. 286.

PLATE II.


Per cent. Coal-Gas in surrounding atmosphere
Per cent. Methane in surrounding atmosphere
0·5
0·5
1·0
1·0
2·0
2·0
2·5
2·5
3·0
3·0

Flame Caps. (Whalley and Tweedie.)
(From the *Transactions of the Institute of Mining Engineers.*)

Limits of Inflammability

If the proportion of combustible gas in such a mixture be increased, a point is reached when flame will be propagated progressively throughout the mixture without the necessity of the continued presence of the source of ignition. And an inflammable or explosive mixture may be defined as one through which flame can be propagated indefinitely, independently of, and away from, the original source of ignition. Inflammability is thus a property of the mixture itself, dependent only on its composition, temperature and pressure, and independent of the shape and size of the vessel containing it.

In the case of mixtures of any particular combustible gas and air (or oxygen) there are, under given physical conditions, certain limits of composition within (but not outside of) which self-propagation of flame will take place after ignition has once been effected. These limits, defined in terms of the percentage of combustible gas present, are usually referred to as the 'lower' and 'higher' limits of inflammability, respectively, of the gas under given conditions. For any particular gas, however, they vary slightly with the position of the source of ignition, since the progress of the flame may be assisted or retarded by convection currents, according as it has to pass in an upward or downward direction. Thus, for example, for methane-air mixtures, at atmospheric temperature and pressure, the limits for different propagation directions are as follows:

	Direction of Propagation.			
	Upward.	Horizontal.	Downward.	
Lower limit - -	5·40	5·40	6·00	per cent.
Higher limit - -	14·80	14·30	13·40	methane in air

In the year 1914 H. F. Coward and F. Brinsley published * the results of some experiments upon the lower limits for hydrogen, methane and carbon monoxide in air, which threw considerable light upon the behaviour of such limiting mixtures. They used, as the containing vessel, a rectangular enclosure of 30 cm. square section and 1·8 metres length, with two opposite sides of wood and two of plate glass. The top was of wood, and the bottom, which was made open, could be closed by a shallow water seal, when the vessel was fixed vertically for the experiments. A small flame of pure hydrogen, introduced near the bottom of the vessel, was used as the source of ignition. Photographs were taken of the flames passing through various 'lower limit' mixtures, which were found to be as follows, each being at atmospheric pressure and saturated with water vapour at 17° to 18° C. :

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* *Trans. Chem. Soc.* **105** (1914), p. 1859–1885.

	Per cent.	
Hydrogen	4·1	in air.
Methane	5·3	
Carbonic oxide	12·5	

Incidentally, it was observed that something very like rings of flame were propagated through such mixtures, and that weak hydrogen-air mixtures (*e.g.* containing between 4·1 and 10 per cent. of hydrogen) will propagate flame indefinitely, but leaving unburnt a considerable fraction of the combustible.

R. V. Wheeler and his collaborators have determined the limits of inflammability of a large number of combustible gases with air, at atmospheric temperatures and pressures, in connection with the work of the Safety of Mines Committee, and the following summary of their results will suffice for our purpose. For all but hydrogen and carbon monoxide, the criterion of inflammability was propagation of flame through a 2½-litre sphere with central ignition. The figures for hydrogen and carbon monoxide refer to upward propagation of flame.

Table XVIII.—Ranges of Inflammability of Gas and Vapour Mixtures with Air (Wheeler)

Gas.	Lower Limit. Per cent.	Upper Limit. Per cent.
Hydrogen	4·1	71·5
Carbon monoxide	12·5	73·0
Methane	5·6	14·8
Ethane	3·1	10·7
Propane	2·2	7·4
Butane	1·7	5·7
Pentane	1·4	4·5
Ethylene	3·0	22·0
Acetylene	3·3	52·3
Vapour.		
Benzene	1·5	5·6
Toluene	1·4	5·4
Ethyl alcohol	4·4	—
Ethyl ether	2·0	5·0
Acetone	2·25	9·6
Carbon disulphide	4·2	—

In 1922 A. G. White, working in Nobel's Research Department, published the results of extended experiments upon the limits for flame propagation in various vapour-air mixtures at atmospheric temperature and pressure, using glass tubes of varying diameters up to 7·5 cms. Several new points of interest were established. In some cases the tubes were closed at both ends (' closed firing '), but in others, one of the ends, either nearest to or remotest from the firing electrodes (=' backward ' or ' forward ' firing respectively) was open and the other closed. This made some difference, especially in the case of ether-air mixtures which, for ' forward firing,' shewed two distinct ranges of horizontal flame propagation (1·88 to 9·45 and 19·0 to 34·0 per cent.), separated by a range which would not propagate flame, the higher of the two ranges relating to a ' cool flame ' of incomplete combustion. Acetaldehyde vapour also similarly exhibited two distinct ranges of inflammability, the ' cool ' flame not being propagated downwards.

It was also observed that " whether a flame was extinguished in, or traversed, certain vapour-air mixtures seemed to depend on the type of flame started, which was generally governable by varying the means of ignition." The cooling effects of the walls did not appear to be important in tubes of 7·5 cm. diameter, and, except in two cases, the lower limits did not differ greatly with the direction of propagation. Albeit, the upper limits for upward propagation were generally much greater than for downward propagation. It was also found that, for all except one of the vapours examined, the lower limit for downward propagation was approximately inversely proportional to the net calorific value of the vapour. Also, the amount of vapour in a lower limit mixture (downward propagation) was about 0·57 of that present in a theoretically perfect combustion mixture, whilst the ratio for the corresponding upper limit was just under 2.

The following are some of White's results for combustible vapour-air mixtures in a glass tube 7·5 cm. in diameter, at atmospheric pressure:

TABLE XIX.—RANGES OF INFLAMMABILITY OF VAPOUR-AIR MIXTURES (WHITE)

Vapour.	Limits of Propagation.	
	Upward.	Downward.
Ethyl ether	1·71 to 48·0	1·85 to 6·40
Acetone	2·89 to 12·95	2·93 to 8·60
Benzene	1·41 to 7·45	1·46 to 5·55
Toluene	1·27 to 6·75	1·28 to 4·60
Methyl alcohol	7·05 to 36·5	7·45 to 26·5
Ethyl alcohol	3·56 to 18·0	3·75 to 11·5
Carbon disulphide	1·06 to 50·0	1·91 to 35·0

In 1924 White published the results of further experiments in which he had studied the influences of both tube diameter and direction of flame propagation upon the ranges of explosibility of mixtures of air with a considerable number of different combustible gases. These are shewn in the following Table XX., in which are given, in the horizontal spaces opposite each gas, its 'lower' and 'upper' limit of inflammability at atmospheric pressure and temperature for tubes of 7·5, 5·0 and 2·5 cms. diameter, respectively, as well as for upward (U.), horizontal (H.), and downward (D.) flame propagation, respectively:

TABLE XX.—RANGES OF INFLAMMABILITY (WHITE)

Shewing the ranges that would propagate flame in different gas-air mixtures in glass tubes of various diameters at 17 ± 3° C.

Gas.	7·5 cm. Tube.			5·0 cm. Tube.			2·5 cm. Tube.		
	U.	H.	D.	U.	H.	D.	U.	H.	D.
Hydrogen	4·15 (4·00) — 75·0	6·50 — —	8·8 — 74·5	4·15 — 74·5	6·70 — —	9·0 — 74·0	4·25 — 73·0	7·15 — —	9·4 — 71·5
Carbon monoxide	12·8 — 72·0	13·6 — —	15·3 — 70·5	13·1 — 72·0	14·1 — —	15·7 — 70·5	13·2 — 71·0	15·9 — —	16·3 — 70·0
Hydrogen disulphide	4·30 — 45·5	5·30 — 35·0	5·85 — 21·3	4·40 — 44·5	5·40 — 26·6	6·05 — 19·8			
Methane	5·35 — 14·85	5·40 — 13·95	5·95 — 13·35	5·40 — 14·25	5·65 — 13·95	6·12 — 13·25	5·80 — 13·20	6·20 — 12·90	6·30 — 12·80
Ethane	3·12 — 14·95	3·15 — 12·85	3·26 — 10·15	3·15 — 14·8	3·22 — 11·75	3·32 — 10·0			
Pentane	1·42 — 8·0	1·44 — 7·45	1·48 — 4·64	1·43 — 8·0	1·46 — 6·70	1·49 — 4·56			
Ethylene	3·02 — 34·0	3·20 — 23·7	3·33 — 15·5	3·13 — 33·3	3·25 — 22·4	3·42 — 15·3	3·15 — 27·6	3·30 — 14·0	3·45 — 13·7
Propylene	2·18 — 9·7	2·22 — 9·3	2·26 — 7·40	2·21 — 9·6	2·26 — 8·4	2·29 — 7·2			
Butylene	1·70 — 9·0	1·75 — 9·0	1·80 — 6·25	1·80 — 9·0	1·82 — 7·4	1·84 — 6·10			
Acetylene	2·60 — 80·5	2·68 — 78·5	2·78 — 71·0	2·60 — 78·0	2·68 — 78·0	2·80 — 63·5	2·73 — 70·0	2·87 — 59·5	2·90 — 55·5

The Effect of Incombustible Gases

The work of R. V. Wheeler and his collaborators has shewn that the effect of a reduced oxygen content of the 'atmosphere' with which a combustible gas is mixed has a marked effect in lowering the upper limit of inflammability, although it does not raise the lower limit nearly to the same extent. This is shewn by the following figures for methane, at atmospheric temperature and pressure, in admixture with atmospheres of varying nitrogen-oxygen contents :

TABLE XXI.—INFLUENCE OF REDUCED OXYGEN-CONTENT OF AIR ON THE RANGE OF INFLAMMABILITY (WHEELER)

Atmosphere.		Per cent. Methane at the	
Oxygen per cent.	Nitrogen per cent.	Lower Limit.	Higher Limit.
20·90	79·10	5·60	14·82
17·00	83·00	5·80	10·55
15·82	84·18	5·83	8·96
14·86	85·14	6·15	8·36
13·90	86·10	6·35	7·26
13·45	86·55	6·50	6·70
13·25	86·75	No mixture capable of propagating flame at atmospheric temperature and pressure.	

In 1926 the Safety of Mines Research Board published a paper, No. 19, containing the results of an investigation upon the influence of black-damp (a mixture of nitrogen and carbon dioxide) upon the inflammability of fire-damp (methane) in air. As might be expected, the extinctive power of carbon dioxide exceeds that of nitrogen, volume for volume. A monatomic gas such as argon or helium has proportionately a less extinctive power than the diatomic nitrogen, helium being more potent than argon owing to its greater thermal conductivity. This aspect of the subject has been further investigated by H. F. Coward and F. J. Hartwell who concluded that, as might be expected, the factors responsible for the extinctive powers shewn by such gases when added to methane-air mixtures are chiefly (i) the reduction of oxygen content of the mixture by the added diluent, (ii) its thermal capacity, and (iii) its thermal conductivity.*

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* *Trans. Chem. Soc.* 1926, pp. 1522–1533.

Limits for Oxygen-Mixtures

As might be expected, at atmospheric temperatures and pressure, the limits for gas-oxygen are generally wider than those for the corresponding gas-air mixtures, as the following figures indicate :

TABLE XXII.—RANGES OF INFLAMMABILITY OF GAS-OXYGEN MIXTURES

Mixtures.	Percentage of Combustible Gas at the Limits of Inflammability.		Author.
	Lower.	Upper.	
Hydrogen-oxygen	9·4	91·0	Le Chatelier
Carbonic oxide-oxygen	15·4	94·1	Do.
Methane-oxygen	6·0	57·3	Do.
Do.	5·7	59·2	W. Payman

With regard to methane, W. Payman,* who in 1919 determined at atmospheric temperature and pressure the limit mixture for methane in various nitrogen-oxygen atmospheres, found that whereas the lower limit was hardly affected, the upper was rapidly raised as the oxygen-content increased, as follows :

TABLE XXIII.—INFLUENCE OF INCREASED OXYGEN CONTENT OF AIR ON THE RANGE OF INFLAMMABILITY (PAYMAN)

Percentage of Oxygen in Atmosphere.	Percentage Composition of Limit Mixture.					
	Lower.			Upper.		
	CH_4.	O_2.	N_2.	CH_4.	O_2.	N_2.
21·0	5·8	19·8	74·4	13·3	18·2	68·5
33·0	5·8	31·4	62·8	25·1	25·0	49·9
50·0	5·8	47·1	47·1	38·8	30·6	30·6
66·0	5·8	62·8	31·4	47·5	35·0	17·5
100·0	5·7	94·2	—	59·2	40·8	—

Also, E. Terres † determined the limits for several combustible gases in atmospheres of air and pure oxygen, respectively, for 'downward' propagation at atmospheric temperature and pressure in a Bunte burette 19 mm. in diameter. The mixtures were ignited from above, and in each case analyses were made to see that the resulting flame had passed through the whole of the mixture. The following were the principal results :

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* *Trans. Chem. Soc.* 115 (1919), p. 1438.

† *Jour. Gasbeleucht.* 63 (1920), 785, 805, 820 and 836.

TABLE XXIV.—RANGES OF INFLAMMABILITY OF GAS-OXYGEN MIXTURES (TERRES)

Gas.	Limits of Inflammability in Air		Oxygen.	
	Lower. Per cent.	Upper. Per cent.	Lower. Per cent.	Upper. Per cent.
Hydrogen - - -	9·5	65·2	9·2	91·6
Carbonic oxide - -	15·6	70·9	16·7	93·5
Methane - - -	6·3	11·9	6·5	51·9
Ethane - - -	4·2	9·5	4·1	45·8
Ethylene - - -	4·0	14·0	4·1	61·8
Acetylene - - -	3·5	52·3	3·5	89·4

Effect of Temperature

As it seems reasonable to suppose that, in general, the limits of inflammability of a particular series of gas-air mixtures would be reached when the amount of heat imparted to, and contained in, the products of combustion of any given layer of it is just sufficient to raise the adjacent layer to its ignition temperature, it may be expected that, *ceteris paribus*, an increase in temperature would widen the limits. This was shewn to be true for the lower limit mixture of methane and air by Taffanel in 1913, whose results were confirmed by Burrell and Robertson three years later. In 1918 W. Mason and R. V. Wheeler found that progressive increases in the temperature from 20° to 700° C. had the following effects upon the limits of inflammability of methane-air mixtures at atmospheric pressure, and for downward flame propagation :

Initial Temperature. °C.	Per cent. Methane in Limit Mixture for Downward Flame Propagation. Lower.	Upper.
20°	6·0	13·40
100°	5·45	13·50
200°	5·05	13·85
500°	3·65	15·35
700°	3·25	18·75

In 1925 A. G. White published,* from Nobel's Research Laboratories, the following results of his experiments upon the ranges of various gas-air mixtures which will propagate flame downwards at different temperatures, up to 400° C. in a tube 25 mm. in diameter.

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* *Trans. Chem. Soc.* 127 (1921), p. 672.

TABLE XXV.—INFLUENCE OF INITIAL TEMPERATURE ON RANGES OF INFLAMMABILITY OF GAS-AIR MIXTURES (WHITE)

Combustible Gas.	Hydrogen.	Carbonic Oxide.	Methane.	Ethylene.	Acetylene.
Temperature °C.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
17°	9·4–71·5	16·3–70·0	6·3 –12·9	3·45–13·7	2·90–55·0
100°	8·8–73·5	14·8–73·7	5·95–13·7	3·20–14·1	2·68–65·0
200°	7·9–76·0	13·5– —	5·50–14·6	2·95–14·9	2·39–81·0
300°	7·1–79·0	12·4–75·0	5·10–15·5	2·75–17·9	2·19– —
400°	6·3–81·5	11·4–77·5	4·80–16·6	2·50– —	— —

Effects of Pressure

In 1914 Terres and Plentz * found that an increase in pressure from 1 to 10 atmospheres somewhat narrowed at each end the range of explosibility of mixtures of air with hydrogen or carbonic oxide, respectively. In the case of methane, however, the range was slightly widened, in the sense of the higher limit being raised a little more than the lower. Their data refer to downward propagation in a closed cylindrical vessel of 8 cms. diameter.

TABLE XXVI.—EFFECT OF INITIAL PRESSURE ON RANGES OF EXPLOSIBILITY AT ATMOSPHERIC TEMPERATURE (TERRES AND PLENTZ)

Mixtures.	1 Atmosphere. Per cent. Combustible Gas.	10 Atmospheres. Per cent. Combustible Gas.
Hydrogen-air - -	9·0 to 68·5	9·5 to 67·5
Carbonic oxide-air -	15·9 to 72·9	18·4 to 62·4
Methane-air - -	6·0 to 13·0	6·6 to 14·0

In 1918 W. Mason and R. V. Wheeler † confirmed Terres and Plentz's observations as regards methane-air mixtures for an increase in pressure of from 1 to 6·1 atmospheres, thus :

Ranges of Inflammability (Percentages of Combustible Gas) for Methane-air Mixtures at :

1 Atmosphere.	6·1 Atmospheres.
6·0 to 13·1	6·4 to 14·05

Subsequently W. Payman and R. V. Wheeler extended such observations to other hydrocarbon-air mixtures over nearly the same pressure range with the following results, which shewed the general effect of pressure to be substantially the same as in the case of methane-air mixtures.*

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* *Jour. Gasbel.* 57 (1914), pp. 995, 1001, 1016, 1025.

† *Trans. Chem. Soc.* 113 (1918), p. 45.

TABLE XXVII.—INFLUENCE OF PRESSURE ON RANGES OF INFLAMMABILITY (PAYMAN AND WHEELER)

Mixtures.	1 Atmosphere. Per cent. Combustible Gas.	6 Atmospheres (approx.). Per cent. Combustible Gas.
Ethane-air - - -	3·13 to 9·95	3·22 to 11·16
Propane-air - -	2·40 to 6·69	2·44 to 7·49
Butane-air - - -	1·92 to 5·50	1·92 to 6·00
Pentane-air - -	1·77 to 4·68	1·68 to 5·42

Effects of High Initial Pressure

During the researches upon gaseous combustion at high pressures which the authors have carried out with Dr. D. M. Newitt since the year 1920 at the Imperial College, London, the effects of pressure upon the ranges of explosibility of various gas-air mixtures in a spherical bomb have been studied over a much wider range of initial pressure than any previous investigators have contemplated. Up to the present the following data have been established for initial pressures of 10, 50, and 125 atmospheres respectively:

TABLE XXVIII.—RANGES OF EXPLOSIBILITY AT HIGH INITIAL PRESSURE (BONE AND NEWITT)

Mixture.	10 Atmospheres.	50 Atmospheres.	125 Atmospheres.
Hydrogen-air - -	9·9 to 67·3	9·9 to 73·3	10·0 to 75·0
Carbonic oxide-air -	16·2 to 66·3	20·3 to 57·8	23·1 to 52·3
Methane-air - - -	5·8 to 17·0	5·7 to 29·5	5·7 to 45·4

It would thus seem that whereas the range for carbon monoxide-air mixtures is considerably narrowed at both ends, the ranges of hydrogen-air mixtures and of methane-air mixtures are both widened at the higher limit, as the initial pressure increases.

Complex Mixtures of Inflammable Gases

In the case of complex combustible gases (such as coal gas, water gas, producer gas and the like), Le Chatelier proposed the following general rule for calculating these limits of inflammability in admixture with air.

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* *Trans. Chem. Soc.* 121 (1922), 2561 and 127 (1925), p. 48.

If a, b, c are the relative proportions of its combustible components, and A, B, C, . . . their respective limits of inflammability, then L, the limit for the mixture will be :

$$L=\frac{a+b+c}{\frac{a}{A}+\frac{b}{B}+\frac{c}{C}}.$$

It will be seen that this formula involves the assumption that the admixture of one limit mixture with another of the same type does not affect the combustion and flame propagation as a whole. In most cases, doubtless, this is so nearly true for combustible gas-air 'limit' mixtures that it may pass muster as a useful empirical rule, although it seems doubtful whether it applies to 'upper limits' in cases where one combustible gas interferes with the combustion of another.

Recently A. G. White has thoroughly tested it out in an exhaustive series of experiments upon both vapour-air and gas-air mixtures of various sorts.* He concluded that " a fair approximation to the value of the limit for a binary mixture can be obtained from the limits of the separate gases by the use of Le Chatelier's rule. The approximation is generally better for lower than for upper limits, and better for downward propagation than for upward. The deviations from this rule are considerably greater for the gas mixtures examined than for normal vapour mixtures, but no rule can be given for the direction of the deviation from the calculated values. For gas as for vapour mixtures, the *type* of flame started sometimes determines whether propagation occurs or no."

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* *Trans. Chem. Soc.* 121 (1922), 2561, and 127 (1925), p. 48.

CHAPTER XI

THE INITIAL PHASES OF GASEOUS EXPLOSIONS

Mallard and Le Chatelier's Researches

Up to about the year 1880 no one believed that, after ignition, flame can be propagated through explosive gaseous mixtures other than at such comparatively slow rates as had been observed by Bunsen in 1857 (*vide* Chapter VI, p. 39); but certain features of a disastrous explosion which occurred in a large gas-main near Tottenham Court Road, London, in that year afforded evidence of the flame having travelled at a speed exceeding 100 yards per second.

In the year 1883, however, the publication of Mallard and Le Chatelier's * classical "*Recherches Experimentales et Théoriques sur le Combustion des Melanges Gaseux Explosifs*," corrected many previous misconceptions and put the matter in a wholly new light. It was henceforth recognised that gaseous explosions pass through certain well-defined stages, commencing with a comparatively slow flame propagation, which soon is accelerated, and culminating in the phase of maximum high speed and intensity known as 'detonation,' as discovered by Berthelot and Vieille in 1881.† In this chapter we will confine our attention to the initial phases of explosions, leaving the discussion of 'detonation' to a later one.

Mallard and Le Chatelier, whose memoir should be carefully studied in detail by every student of explosions, tried four different methods for measuring flame speeds, of which only two need be mentioned here. The first of these was based upon the well-known fact that the gap between two wires across which an electrical spark will jump in a gaseous medium is much greater at flame temperatures than in the cold. It consisted in arranging two or more spark-gaps, connected with an induction coil and battery at suitable distances along a horizontal tube containing an explosive mixture, the dimension of the gaps being such that the spark could not pass whilst the medium was cold. As soon, however, as the mixture was ignited and the flame reached the first gap a spark passed across it at each interruption of the primary current; simultaneously a feeble current traversed the induction coil, and it was utilised for registering a mark on a chronographic arrangement. In this way the time interval taken by the flame front traversing the distance between two successive gaps was measured. The chronographic arrangement employed was a metallic cylinder rotated at a uniform peripheral speed of 1 metre per second. And, as the induction coil used gave 100 interruptions per second, the possible error in measurement would not exceed $\frac{1}{100}$th second.

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* *Annales des Mines*, 8, Sér. iv. (1883), pp. 274–618.

† *Ann. de Phys. et Chim.* 28, Sér. v. (1881), p. 289.

The method which Mallard and Le Chatelier considered the best of all, because it permitted of the whole flame movement being studied and not merely its average speed between two given points, consisted essentially in recording photographically the movement of the flame along a horizontal glass tube on a sensitised plate moving vertically at a known uniform velocity, thus obtaining a graph compounded of the two velocities, from which the flame velocity at any point could be deduced. They employed horizontal tubes (of diameters usually between 1 and 3 cms.) in sections each 1 metre long, connected in series by means of caoutchouc rings. The whole was focussed, by means of a wide aperture lens, on a vertical plate moving at a known uniform velocity of about 1 metre per second. Time intervals were also registered on the plate by interrupting 100 times per second a beam of 'magnesium' light focussed on another part of the plate. In this way, to quote the original memoir, "*On obtiendra une courbe dont chaque point aura pour abscissa le chemin parcouru par la flamme dans la tube, et pour ordonné le temps écouté depuis l'origine de la combustion.*"

As the plates used by Mallard and Le Chatelier were not sufficiently sensitive to afford satisfactory records with flames such as those yielded by mixtures of either hydrogen or carbonic oxide with oxygen, they employed explosive mixtures of carbon disulphide with either oxygen or nitric oxide whose flames are much more actinic, on the supposition that such might be regarded as typical of 'oxygen' or 'air' mixtures respectively.

The behaviour of these mixtures was found to differ according as they were ignited at or near (*a*) the *open*, or (*b*) the *closed* end of a tube. In the case of (*a*) it was always observed that the flame proceeded for a certain distance along the tube at a practically uniform slow velocity, which Mallard and Le Chatelier regarded as the true rate of propagation 'by conduction.' With CS_2+6NO mixtures this uniform movement was succeeded by an 'oscillatory period,' the flame swinging backwards and forwards with increasing amplitudes, and finally *either* dying out altogether, *or* giving rise to 'detonation,' according to circumstances. With the 'oxygen' mixtures the initial period of uniform velocity was shorter, and appeared to be succeeded abruptly by 'detonation,' without passing

PLATE III.

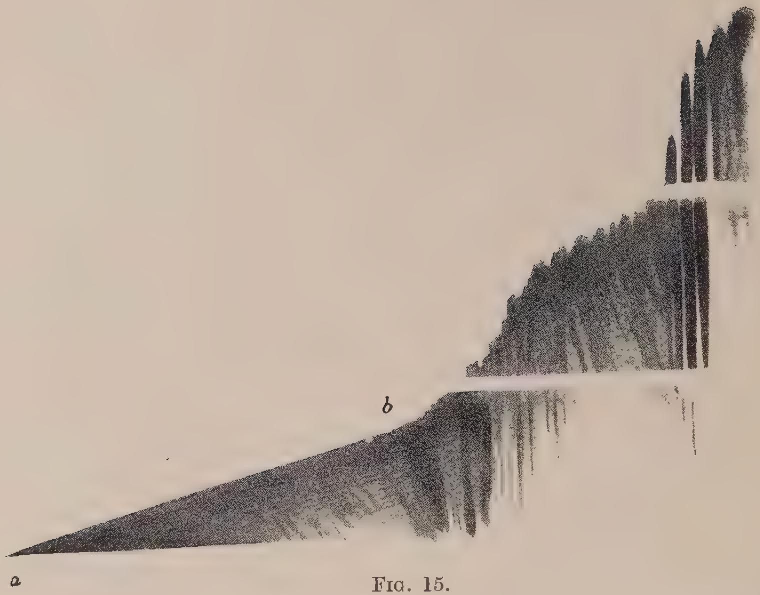

FIG. 15.

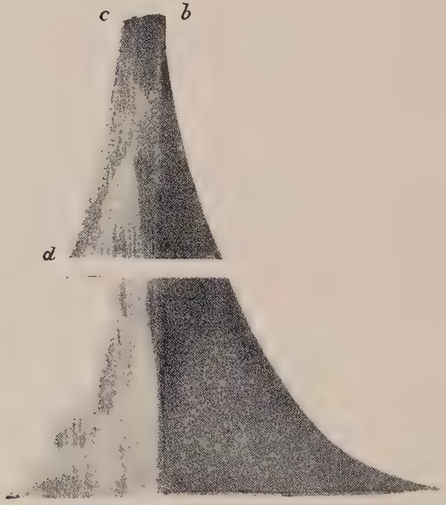

FIG. 17.

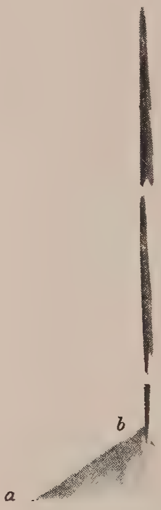

FIG. 16.

MALLARD AND LE CHATELIER'S PHOTOGRAPHIC RECORDS OF FLAME MOVEMENTS THROUGH GASEOUS EXPLOSIVE MEDIA IGNITED IN GLASS TUBES.

through any intermediate 'oscillatory period.' When, however, the mixtures were ignited near the *closed* end of the tube, the forward movement of the flame was continuously accelerated until finally 'detonation' was set up.

These important features of their experiments are well shewn in Figs. 15 to 17 respectively (Plate III), which need no further explanation. Fig. 15 is the graph from the explosion of a mixture CS_2+6NO in a tube 3 cms. in diameter and 3 metres long composed of three sections, each 1 metre long, connected in series by means of caoutchouc rings which in the graph serve as reference marks, ignition having been effected near the *open* end. Here the portion *ab* of the graph shews the 'initial uniform movement' which lasted until the flame had traversed nearly all the first metre section of the tube, whilst the remainder shews the 'oscillatory period' which extended over the next $1\frac{3}{4}$ metres or so, when the flame was extinguished. Fig. 16 shews the graph from a CS_2+3O_2 explosion in a tube, 1 cm. in diameter and 3 metres long, ignition having been at the *open* end, in which the initial 'uniform movement,' indicated by the portion *ab*, was abruptly succeeded by 'detonation.' Fig. 17 shews the graph from a CS_2+6NO explosion originated by spark ignition near the *closed* end of a tube 3 cm. diameter and 3 metres long. It was noticed that whereas the initial 'slow uniform movement' exhibited no signs of violence, the final 'detonation' was characterised by an exceedingly high uniform velocity, great brilliance of flame, as well as by the shattering effects usually associated with the popular idea of explosions. The contrasts between these initial and final stages are well brought out in Fig. 16.

The Initial 'Uniform Movement'

Although Mallard and Le Chatelier found the velocity of the initial slow uniform movement to be independent of the material composing the walls of the tube ("*la nature des parois du tube ne parait exercer aucune influence sur la vitesse de propagation . . .*"), they shewed that it may be retarded by their cooling influence unless a certain limiting diameter is exceeded. This 'limiting diameter' seemed not to be fixed but to vary with the composition of the explosive mixture and with the velocity of flame propagation through it. They found that, in general, the limiting diameter necessary to any retardation of the flame is greater the slower the flame-velocity; and, conversely, that the constriction of tube requisite to extinguish the flame is greater the greater the flame-velocity.

The distance along a tube from the point of ignition to which the initial uniform flame-movement will extend in any particular case was found to depend on both the total length and diameter of the tube, within certain limits. Thus, for example, in the case of a CS_2+3NO mixture inflamed in glass tubes of different lengths and diameters, the distance traversed in uniform movement was found to be as follows :

Diameter in cms.		3	2	1	
Length of Tube in metres	1.	0·50	0·56	—	Distance in metres traversed in 'uniform movement.'
	2.	0·80	0·73	0·25	
	3.	1·00	0·72	0·25	

Mallard and Le Chatelier regarded the initial uniform flame-movement through a stagnant explosive mixture as being governed by the transference of the heat of combustion from one layer to the next 'by conduction,' in the sense that hot products streaming out from the burning layer mix with the cold unburnt gases in the next layer, which is thereby raised to its ignition temperature. From such point of view, provided that the tube diameter exceeds the aforesaid limit, and that ignition is at the *open* end of the tube by a source of heat not greatly exceeding in temperature the ignition temperature of the mixture, and does not appreciably disturb it, the speed of the uniform movement would depend only on the composition of the mixture, its temperature and pressure. Thus, for example, Mallard and Le Chatelier obtained the following speeds for various hydrogen-air mixtures at atmospheric temperature and pressure :

Hydrogen (per cent.) - -	6	10	20	30	40	50	60	70
Speed (cm. per sec.) - -	0	60	195	330	437	395	230	110

The general conclusion which Mallard and Le Chatelier drew from this part of their work is best expressed in their own words, as follows : "*C'est que lorsqu'on allume un mélange gazeux explosible avec une flamme, l'inflammation commence toujours au début par se propager d'un mouvement uniform. La vitesse de ce mouvement uniform, qui se prolonge pendant un temps plus ou moins long suivant les cas, est constante pour un même mélange gazeux brûlant dans les mêmes conditions ; elle est toujours modérée et certainement inférieure à 30 mètres par seconde pour tous les mélanges étudiés jusqu'à présent.*"

They proposed the following equation for the velocity of the 'uniform movement' on the supposition that the cold mixture immediately in front of the flame is raised to its ignition temperature by conduction of heat from the burning and burnt layers immediately behind the flame front :

$$V=\frac{L(T-t)}{C(t-\theta)}f(T, t)$$

where T = temperature of combustion,
t = ignition temperature of the mixture,
θ = the initial temperature,
L = the thermal conductivity of the unburnt gas,
C = the mean specific heat of the burning or just burnt gas,
$f(T, t)$ = a constant.

And according to Mason and Wheeler, the speed is, in fact, proportional to $\frac{T-t}{t-\theta}$ with various mixtures of methane, oxygen and nitrogen containing sufficient oxygen for complete combustion. Seeing, however, the almost insuperable difficulties at present involved in determining with sufficient exactitude the precise numerical values to be assigned to the various terms included in the formula, particularly in view of our ignorance of the amount of combustion occurring in the flame front itself in any particular case, it should be received with due reservation.

Le Chatelier (*Leçons sur le Carbone*, pp. 287-9), gave the following curve (Fig. 18) for hydrogen-air mixtures, remarking that the maximum flame velocity for the series is shewn by a mixture (40 hydrogen/60 air) containing more than the theoretical proportion of combustible, adding that "*La vitesse de transmission de la chaleur, de la couche enflammée à la couche froide voisine, et par suite la vitesse de propagation de la flamme, est évidemment d'autant plus grande, d'une part, que la température de combustion est plus élevée et d'autre part, que la conductibilité du mélange est plus grande.*" It should be pointed out, however, that he seems to have considered that the prolongation of the line drawn through the observed speed-ordinates down to the zero in such a diagram would indicate in the abscissa the 'limits of inflammability' for the hydrogen-air series, a procedure which recent research has shewn to be unjustifiable.

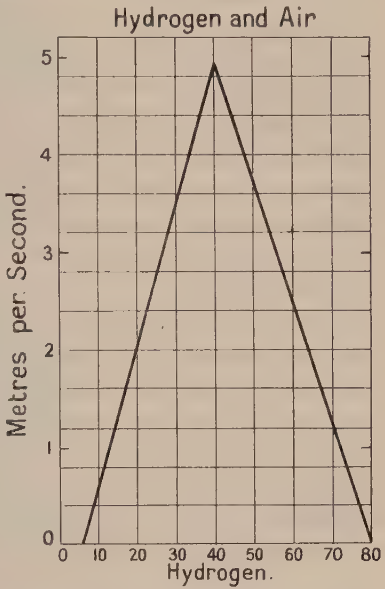

FIG. 18.—SPEED OF 'UNIFORM MOVEMENT' IN HYDROGEN-AIR MIXTURES. (Mallard and Le Chatelier.)

The Oscillatory or Vibratory Movement

Mallard and Le Chatelier recognised that the moderate flame-speeds which characterise the initial uniform movement could be accelerated by such influences as 'turbulence,' which would assist in the transmission of heat; and they attributed the 'vibratory movement,' which in many of their 'open tube' experiments immediately succeeded the initial 'uniform movement,' to the explosive mixture being thrown into a state of rapid vibration as the result of hot burnt gases being ejected by expansion from the open end. Using tubes 1, 2, and 3 metres long, and 1, 2, and 3 cms. in diameter, respectively, they found the vibration-amplitudes, which at first were weak, to increase until they reached a maximum after the flame had traversed between two-thirds and three-quarters of the total length. In cases when the far end of the tube was closed, the vibrations afterwards diminished in amplitude as the flame approached that end. The time-periods of successive vibrations varied, as also did the mean forward rate of flame propagation, which, however, was always greater than that of the uniform movement.

During the ‘ vibratory period ’ the flame may either be extinguished, if during a backward swing it is (so to speak) asphyxiated, or give rise to ‘ detonation,’ if sufficiently accelerated during a forward swing. It was shewn that when extinction occurred it was invariably associated with a backward swing during a vibration of great amplitude ; in such circumstances the extinction might not be final, a new inflammation of reduced intensity supervening. Indeed, the photographic records shewed the combustion intensity to be very variable during different phases of the same vibration.

H. B. Dixon, who used a photographic method similar to that of Mallard and Le Chatelier, in his well-known researches upon the development of explosions up to ‘ detonation,’ which will be more fully discussed in a later chapter, obtained the beautiful record reproduced in Plate IV of the oscillation of flame in a burning mixture of CS_2+8NO between 4 and 5 feet from the firing point down a tube 5 feet long and 1 inch bore. The oscillations shewn were of large amplitude, which reached a maximum at the third swing, where the luminosity was also the greatest.*

R. V. Wheeler's Determinations of Flame Speeds during the Initial Uniform Movement

The researches of R. V. Wheeler and his collaborators since 1914, under the auspices of the Safety of Mines Committee, come next to those of Mallard and Le Chatelier, and have greatly extended our knowledge of the initial slow ‘ uniform movement.’ And, whilst we differ from their interpretation of flame propagation, and shall feel bound in the next chapter to criticise some of their recent conclusions concerning it, we do not desire to detract in the least from the undoubted value of their experimental work.

Wheeler and his collaborators have chiefly used two experimental methods, namely : (i) involving the fusing of very fine copper ‘ screen wires ’ (Fig. 19) fixed in series at regular intervals along the path of the flame, each wire being part of an electric circuit connected with a suitable chronographic recorder, and (ii) a photographic method essentially the same as that employed by Mallard and Le Chatelier.

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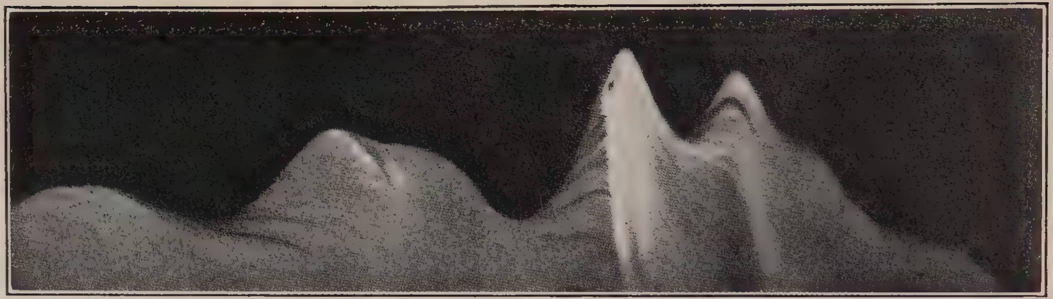
* *Phil. Trans.* A. 200 (1903), p. 346, and Pl. 18, Fig. 68.

PLATE IV.



Oscillations of Flame in a $CS_2 + 8NO$ Mixture. (Dixon.)

In the paper in which his 'screen-wire' method was originally described* Wheeler had no difficulty in shewing that Mallard and Le Chatelier had grievously erred in their methane-air speed curves, partly because of the impurity of the methane employed by them (it had been prepared from sodium acetate),† and partly because of their wrong assumption that the flame velocities for mixtures near the upper and lower limits would

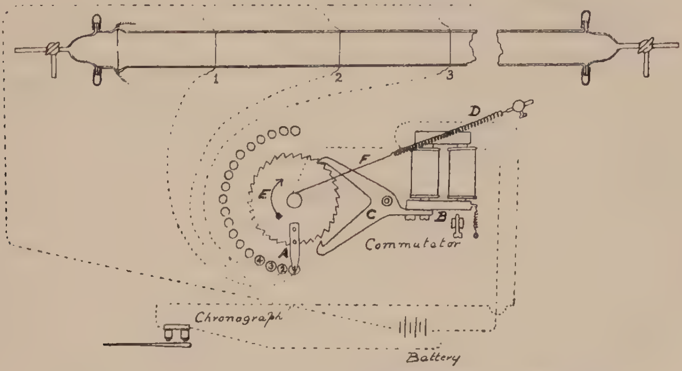


FIG. 19.—R. V. WHEELER'S 'SCREEN-WIRE' APPARATUS.

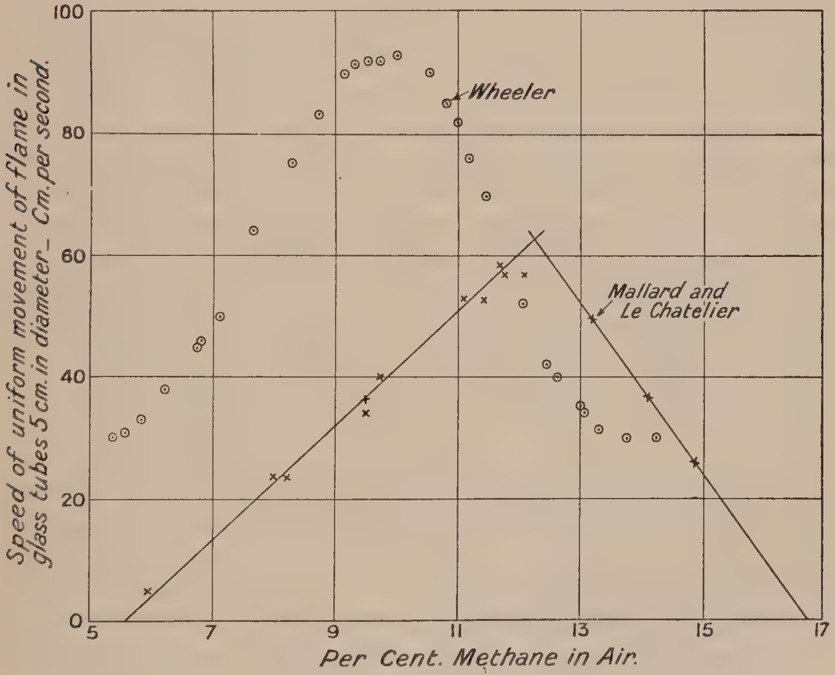


FIG. 20.

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* *Trans. Chem. Soc.* 105 (1914), pp. 2606 to 2613.

† According to Wheeler such methane may contain as much as 10 per cent. of unsaturated hydrocarbons and 2 or 3 per cent. of hydrogen, besides nitrogen.

gradually approach zero as the said limits were attained. Wheeler not only found velocities of about 36 cm. per second for both the upper and lower 'limit-mixtures,' but also shewed that the velocity-curve plotted from his experiments for the whole series of methane-air mixtures was quite different from that plotted from Mallard and Le Chatelier's published results. How great was the difference is shewn in Fig. 20, where the two velocity curves for methane-air mixtures, when ignited near the open end of a glass tube 5 cm. in diameter, are plotted side by side. It will be noticed that whereas Mallard and Le Chatelier found a maximum velocity of 63 cms. per sec. for a mixture containing about 12·2 per cent. of methane, and a rapid falling off in velocity as this composition was deviated from, Wheeler found a maximum velocity of 90 to 92 cm. per second for a series of mixtures containing between 9·5 and 10·5 per cent. of methane. Indeed all subsequent work on the subject has justified Wheeler's contention that Mallard and Le Chatelier went wrong in the form which they gave to their flame-speed curves generally, and his correction of their mistake was most timely.

From later results for methane-air mixtures published by W. Mason and R. V. Wheeler * it would appear necessary to qualify Mallard and Le Chatelier's conclusion that in the initial period of uniform slow movement the flame is propagated from layer to layer by 'conduction' only. For, if such were so, the velocity for a given explosive mixture would be independent of the tube-diameter, as long as the latter exceeds a certain limit at which the walls cease to have any appreciable cooling influence upon the flame. This, however, was shewn by Burgess and Wheeler not to apply to methane-air mixtures when ignited in a series of horizontal tubes of increasing diameters, as is strikingly illustrated in the curves included in Fig. 21. The 'velocity of inflammation,' as it is sometimes called, for any given methane-air mixture increases with the diameter of the tube in far greater measure than can be attributed to diminishing 'cooling influence.'

The late W. A. Haward and T. Otagawa,† working in Wheeler's laboratory, shewed that similar considerations also applied, though in a modified sense, in the case of hydrogen-air mixtures, where the speeds of initial uniform flame movement are much greater than in the case of methane-air mixtures. Employing three tubes, each about 1·5 metres long, but with diameters of 9 mm., 11·5 mm. and 25 mm. respectively, the authors in question obtained results which are plotted in the curves shewn in Fig. 22 for hydrogen-air mixtures at atmospheric temperature and pressure.

Comparing these results with those of Mallard and Le Chatelier for a 10 mm. diameter tube (*vide* Fig. 18) it will be seen that, whereas the latter

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* *Trans. Chem. Soc.* 111 (1917), pp. 1044 to 1057.

† *Trans. Chem. Soc.* 109 (1916), pp. 83 to 89.

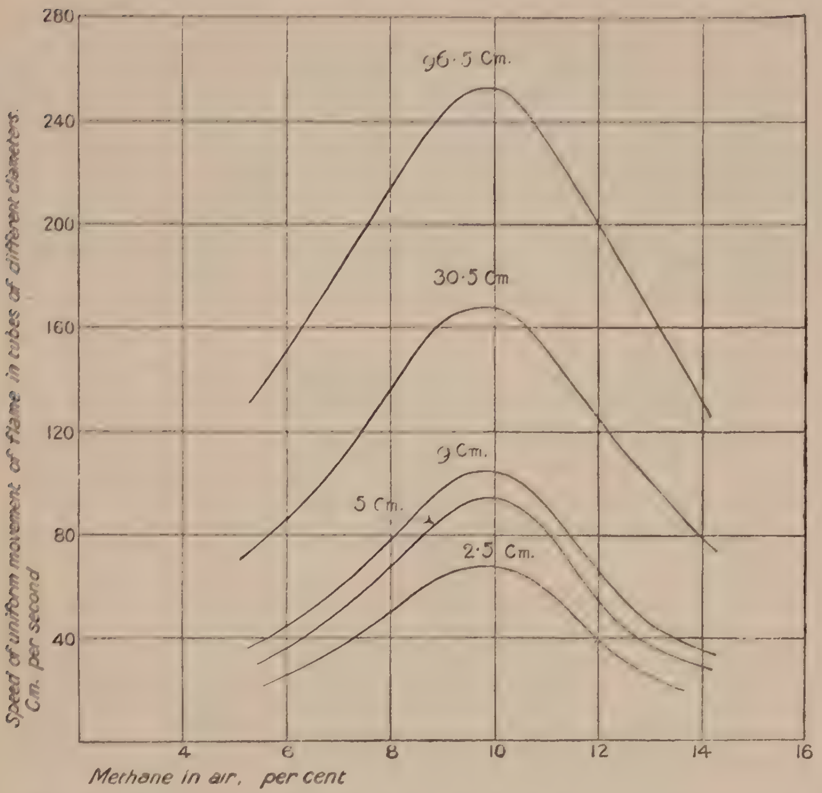

FIG. 21.- INFLUENCE OF TUBE DIAMETER ON SPEED OF UNIFORM MOVEMENT IN METHANE-AIR MIXTURES. (Burgess and Wheeler.)

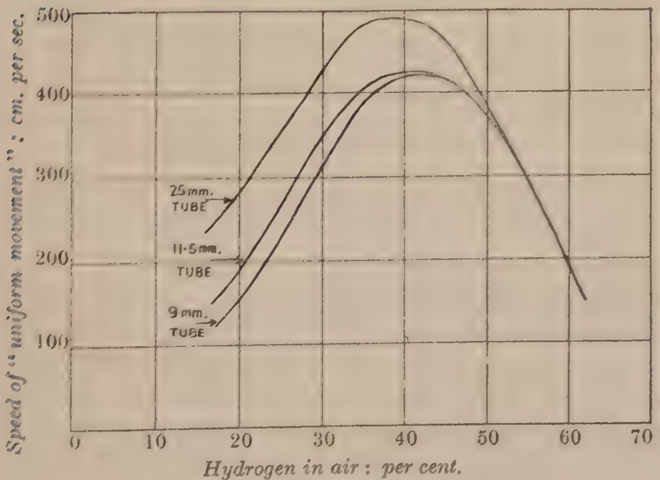

FIG. 22.—SPEED OF 'UNIFORM MOVEMENT' IN HYDROGEN-AIR MIXTURES. (Haward and Otagawa.)

observers had found a very sharply defined maximum speed (437 cm. per sec.) for one particular mixture containing 40 per cent. of hydrogen, Haward and Otagawa found nearly the same 'maximum' speed (400 to 420 cm. per sec.) to apply to all mixtures containing between 38 and 45 per cent. of hydrogen. Moreover, an increase in the tube-diameter brought about a decided increase in the flame velocities of all mixtures between the lower limit of inflammability (H_2=16·0 per cent.) and that containing about 55 per cent. of hydrogen, but not of those containing more of it. In other words, it would seem that only with mixtures containing upward of 55 per cent. (*i.e.* a large excess) of hydrogen does the influence of the tube diameter become negligible.

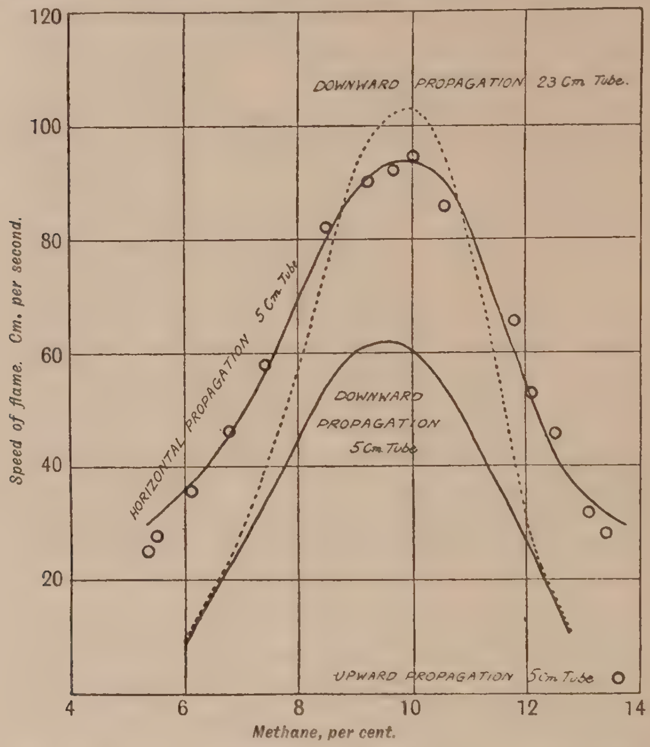

FIG. 23.—INFLUENCE OF DIRECTION OF PROPAGATION ON THE SPEED OF 'UNIFORM MOVEMENT.' (Mason and Wheeler.)

Wheeler and his various collaborators, as well as other recent investigators, have repeatedly shewn that for a given gas-air mixture, under same temperature and pressure conditions, the speed of the initial uniform slow movement depends somewhat on whether propagation be in an upward, downward, or horizontal direction; in other words, it varies somewhat with direction, as might be expected. In 'upward' propagation, convection currents assist, whilst in 'downward' propagation they hinder, propagation. The two curves in Fig. 23 which represent the speeds found by Mason and Wheeler * in the case of methane-air mixtures, at atmospheric temperature and pressure, in a 5 cm. diameter tube, for vertically downward and horizontal propagations, respectively, will suffice to illustrate this point. The difficulties of making similar measurements of flame speeds in a vertically upward direction are considerable, but Wheeler and Mason record (*loc. cit.* p. 1231) that " over the comparatively short period during which the speed of the flame travelling upwards could be regarded as constant, that speed, for any mixture of methane and air, was not greater than during the uniform movement in a horizontal tube ; it was sometimes less."

It may here be said that, whereas it seems probable that ' conduction ' plays an important, and possibly in some cases a predominant, part in the propagation of flame from layer to layer during the initial period of uniform flame movement, other factors, such as convection currents and turbulence, which by producing movements *en masse* of the combining gases quicken the combustion, must also come into operation, more or less according to circumstances. Also, the ' intensity ' of the source of ignition may play a considerable part. Indeed the propagation of the flame during the initial phase of uniform slow movement may not be entirely a thermal phenomenon, as many have hitherto supposed, but thermionic influences may also come in. From this point of view it may perhaps even be doubted whether, strictly speaking, the expression ' flame-speed ' ought to be used in connection with the initial uniform slow movement in the sense of its being a ' natural constant ' for each particular gas-air mixture, so much does it vary with circumstances other than pressure and temperature.

In this connection it is interesting to note that Mason and Wheeler have said regarding the ' uniform movement,' that, " if Le Chatelier's definition of it as ' *le mode de propagation par conductibilité* ' be accepted, it is a strictly limited phenomenon obtainable only in tubes within a certain range of diameter, large enough to prevent appreciable cooling of the walls, but narrow enough to suppress the influence of convection currents—alternatively—(it) . . . should be regarded simply as a particular phase in the propagation of flame that occurs when ignition is effected (in a quiescent mixture) at the open end of a straight horizontal tube (of any diameter) closed at the other end, and not as resulting from a particular mode of heat transference." † It might also be added that the ignition should be by a source of heat not greatly exceeding in temperature the ignition temperature of the mixture, and not productive of mechanical disturbance of the mixture.

In general, it seems reasonable to suppose that the ' flame-speed ' during the initial phase of slow uniform movement may or will depend upon temperature, pressure, tube diameter, convection currents, the mode and intensity of ignition, thermionic effects, and possibly other factors. Probably it is a more complex phenomenon than Mallard and Le Chatelier supposed, and dogmatic assertions concerning it are to be deprecated. To these aspects of the problem we will revert in Chapter XIII, in discussing some recent photographic researches carried out in our own laboratories. Meanwhile, the following 'flame-speed' data for the initial uniform movement through various commonly used gases in admixtures with air may be referred to.

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* *Trans. Chem. Soc.* 117 (1920), pp. 1227 to 1240.

† *Ibid.* p. 1228.

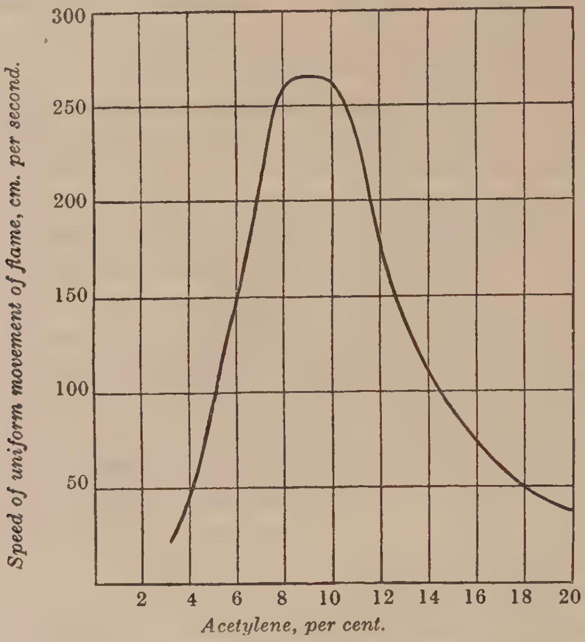

FIG. 24.—SPEED OF 'UNIFORM MOVEMENT' IN ACETYLENE-AIR MIXTURES.
(Haward and Sastry.)

In 1917 the late W. A. Haward and S. G. Sastry published * the curve shewn in Fig. 24 for acetylene-air mixtures at atmospheric temperature and pressure, which differed materially in character from a similar curve published by Le Chatelier in 1895. † The method employed was the 'screen-wire' one already referred to, speeds being measured between two points 40 cm. apart, the first being 10 cm. from the open end of a horizontal tube of 12 mm. diameter. Ignition was by means of a lighted taper, drawn rapidly past the open end. An examination of Haward's note book, now in our possession, has shewn some considerable variations in the speeds observed in successive experiments with a given acetylene-air mixture in one and the same tube, suggesting that they are very sensitive mixtures. The authors in question stated in their paper (*loc. cit.*

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* *Trans. Chem. Soc.* 111 (1917), pp. 840 to 843.

† Compt. rend. 121, p. 1144.

p. 843) that "the speeds in tubes of 9 mm. and 25 mm. diameter were also determined. The speeds in the 9 mm. tube were slower than those obtained in the 12 mm. tube, but the shape of the curve was the same. With the larger tube, 25 mm., the duration of the uniform movement was too short to admit of accurate measurement by the means employed."

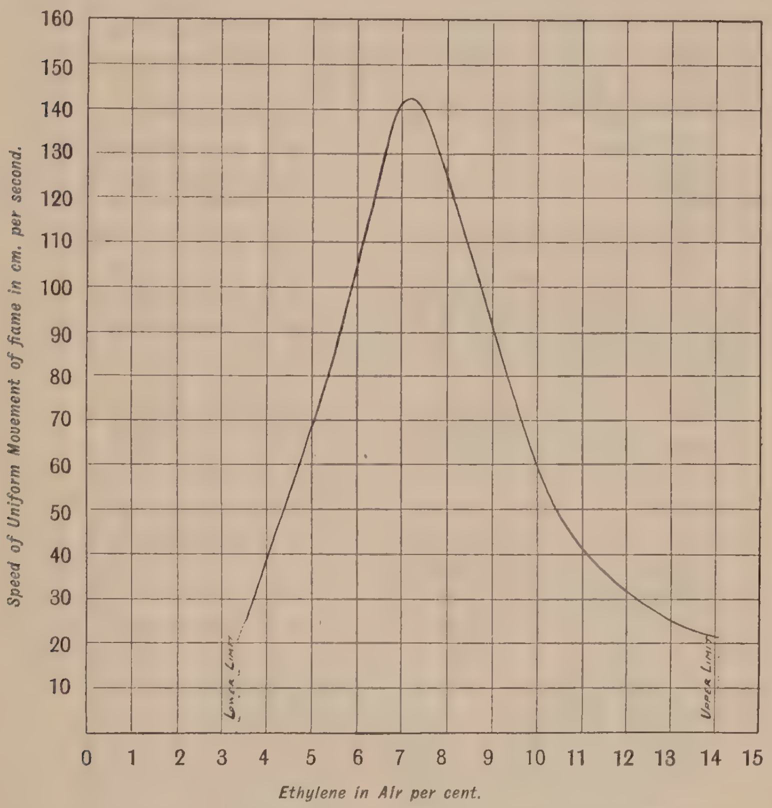

FIG. 25.—SPEED OF 'UNIFORM MOVEMENT' IN ETHYLENE-AIR MIXTURES.
(Chapman.)

A similar curve for ethylene-air mixtures, subsequently published by W. R. Chapman,* who also worked under R. V. Wheeler's direction in the Eskmeals laboratories, is shewn in Fig. 25. He also employed the 'screen-wire' method and a horizontal tube 2·5 cm. in diameter. In the same paper he also published the series of curves shewn in Fig. 26, which summarises in a convenient manner the flame speeds obtained in Wheeler's laboratories for mixtures of air with hydrogen, carbonic oxide (saturated with water at 12° C.), methane, ethane, ethylene, and acetylene respectively, ignited in horizontal glass tubes 2·5 cm. in diameter, all plotted to the same scale for comparison. It should be noted that in the case of

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* *Trans. Chem. Soc.* 119 (1921), pp. 1677 to 1683.

CO-air mixtures the speed varies with their hygroscopic state, the maximum speeds being obtained with 6 per cent. of water vapour.

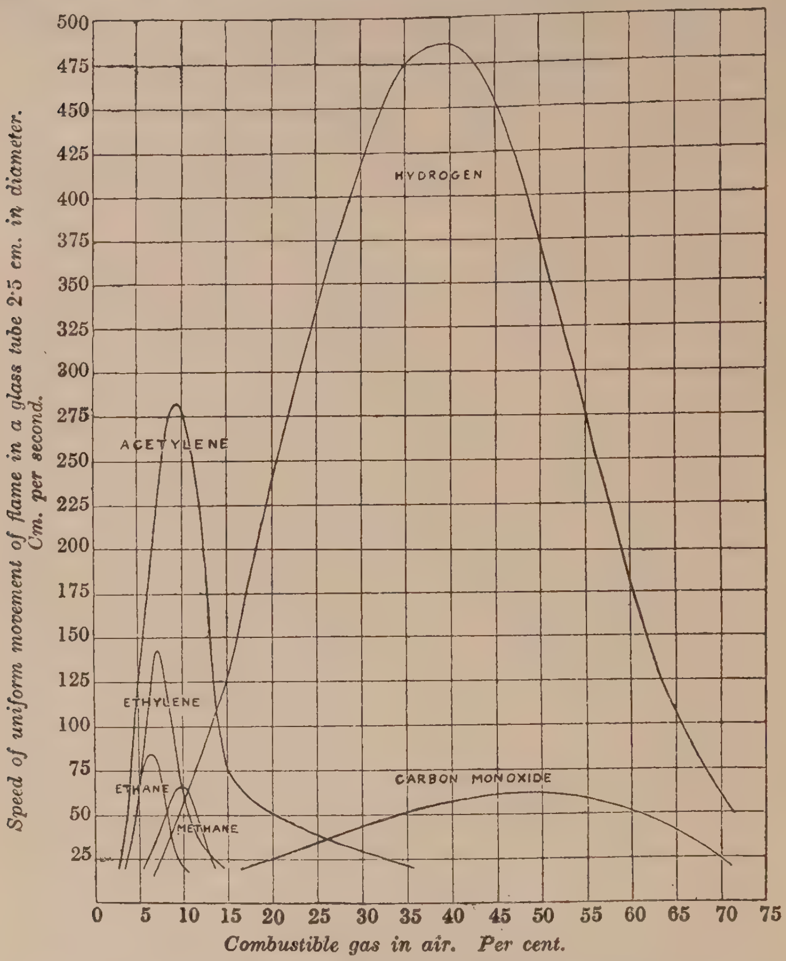
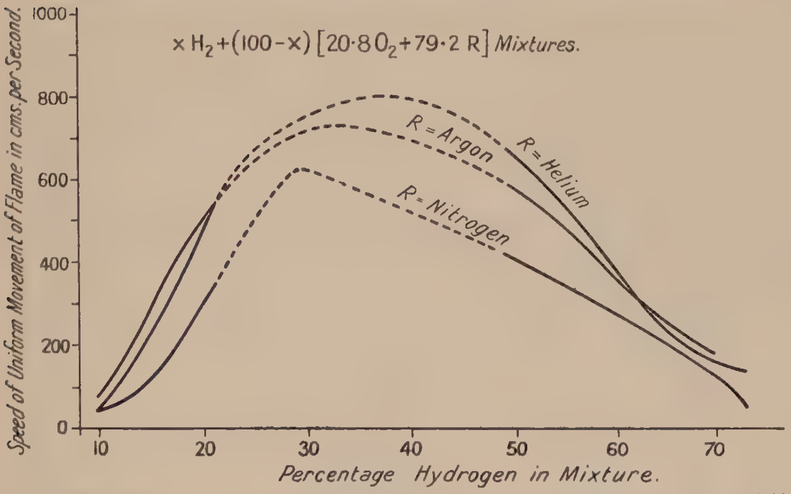


FIG. 26.—COMPARISON OF SPEEDS OF 'UNIFORM MOVEMENT' OF MIXTURES OF VARIOUS COMBUSTIBLE GASES WITH AIR. (Chapman.)

Some Recent Measurements shewing the Effect upon the Speeds of Initial 'Uniform' Movement of replacing the Nitrogen of Hydrogen-Air, Acetylene-Air, and Methane-Air Mixtures by its Equivalent of Argon or Helium respectively

In Figs. 27 and 28 are reproduced some interesting curves embodying results recently obtained by W. A. Bone, R. P. Fraser and D. A. Winter at the Imperial College, London, in experiments in which the nitrogen of various hydrogen-air and acetylene air mixtures, respectively, was replaced by its equivalent volume of argon or helium respectively. All the



Note.—*Dotted portions of curves represent mean of values which were found to be somewhat variable.*

Fig. 27.—Relative Influences of Helium, Argon and Nitrogen on the Speed of 'Uniform Movement' in Hydrogen Mixtures. (Bone, Fraser and Winter.)

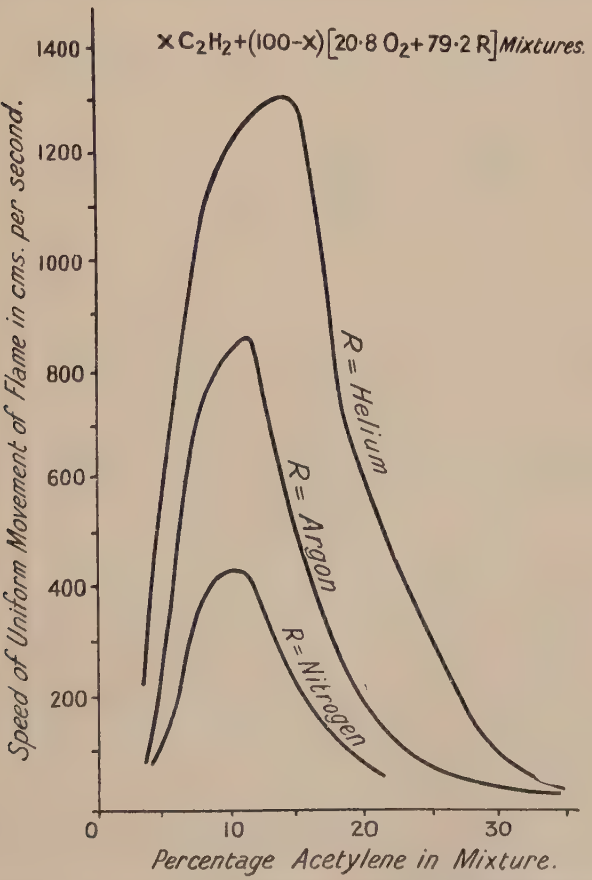


Fig. 28.—Relative Influences of Helium, Argon and Nitrogen on the Speed of 'Uniform Movement' in Acetylene Mixtures. (Bone, Fraser and Winter.)

mixtures were ignited at 15° C., and atmospheric pressure by means of a 2 cm. high coal-gas flame at the open end of a tube 2·5 cm. diameter and of length varying between 30 and 80 cms. In Fig. 29 are reproduced the curves for results similarly obtained by H. F. Coward and B. F. Hess, for methane-air mixtures, also in a tube 2·5 cm. diameter. As might be expected, the replacement of the diatomic nitrogen in a given mixture by either of the two monatomic diluents always raised the speeds of initial flame propagation, helium having a greater effect than argon, probably owing to its greater thermal conductivity. It will also be observed that the effects of such replacements were relatively much greater in the case of the hydrocarbon-air than with the hydrogen-air mixture, a circumstance which suggests the possibility of nitrogen not being so 'inert' a diluent in the former as in the latter mixtures. In this connection it may be stated that definite evidence has been forthcoming from recent experiments made at the Imperial College, London, on the explosion of an acetylene-air mixture, $C_2H_2 + O_2 + 3{\cdot}75N_2$, that the nitrogen is not inert in such cases, a circumstance which we shall have occasion to refer to again in a future publication.

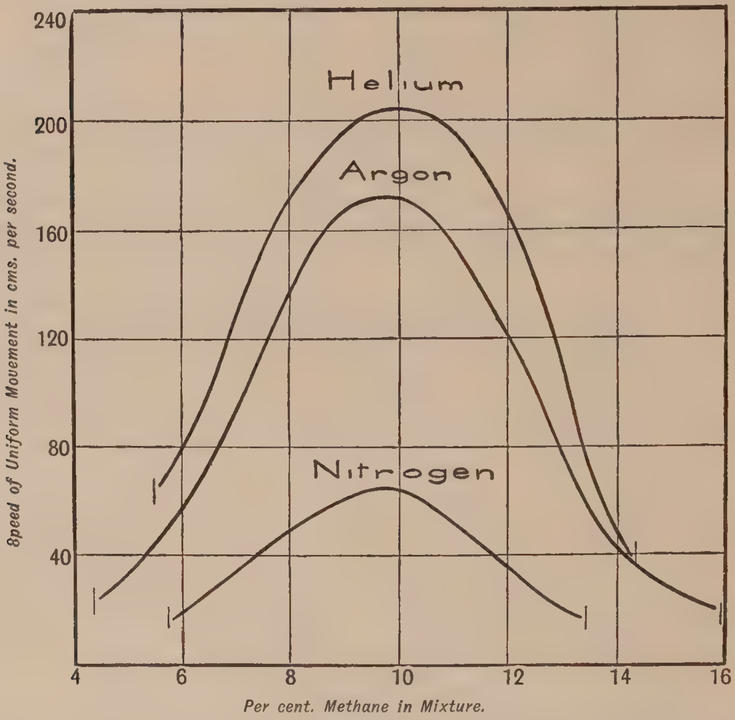


Fig. 29.—Relative Influences of Helium, Argon and Nitrogen in Methane-Oxygen Mixtures on the Speed of 'Uniform Movement.' (Coward and Hess.) (From the *Transactions of the Faraday Society*.)

An Apparatus for Demonstrating Flame Movements *

An apparatus suitable for lecture demonstrations of flame movements during the initial phases of a gaseous explosion, using coal gas-air mixtures for the purpose, is shewn in Fig. 30. It consists of a horizontal glass tube 14 ft. long and 1½ inches internal diameter (the exact dimensions do not matter much), open at both ends; it may be conveniently built up in three sections connected by rubber joints. At one end, and in alignment with its axis, is fixed either a Teclu burner or the burner device shewn in the diagram, in such a way that, either by suitably altering the adjustment of its primary air-supply, or by moving the position of the orifice of the burner in relation to the opening of the tube, any explosive mixture of gas and air between the 'limits of inflammability' can be made to flow through the tube. Indeed, after a little practice, a careful operator will soon learn how to make the adjustment necessary to produce almost any desired explosive mixture. Near the other end are fitted sparking wires for firing it. Experiments may be made somewhat as follows:

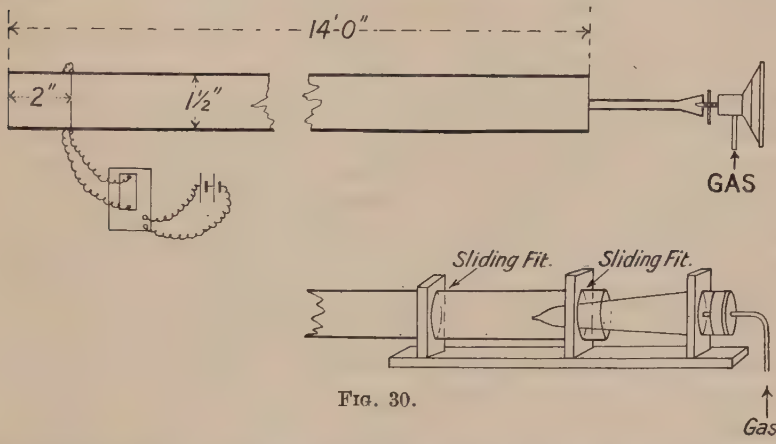


FIG. 30.

(1) If to begin with, such adjustment of the burner is made as to deliver into the tube a mixture containing as little air, but as much coal-gas, as will just allow of its being inflamed by the spark, and sufficient time be allowed for the complete displacement of the air in the tube of the mixture, then, on stopping the flow by turning off the gas and a moment later igniting the stagnant mixture, a pale bluish-green flame will start from the point of ignition and travel quietly at a uniform slow rate the whole way down the tube. The time occupied by the journey from one end to the other will depend somewhat upon the composition of the coal-

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* This apparatus was designed by one of the authors (W. A. B.), to demonstrate flame-movements to a large audience in connection with an Evening Discussion on Flame in the Town Hall, Newcastle-on-Tyne, during the British Association Meeting in that city on the 7th September, 1916, and has been similarly employed by him in other public lectures.

gas used, but it will probably be of the order of 10 seconds. Assuming the coal-gas to be of good quality, the body of the flame will be greenish-blue in colour with a rounded head, and it will probably terminate in a reddish-brown tail, which presumably represents the exothermic adjustment of the 'water-gas equilibrium' ($CO + OH_2 \rightleftharpoons CO_2 + H_2$) in the system with the temperature as the products of combustion cool down from the highest temperature of the flame.

(2) By further suitable adjustments at the burner the proportion of air in the mixture supplied to the tube may be gradually increased. On igniting such an air-richer mixture the velocity at which flame is propagated along the tube will increase noticeably, until, with a certain proportion of air, it reaches a maximum. The flame will now travel much faster than in the first experiment, although not faster than can be followed by an observer's eye; and, after traversing a certain distance at a uniform velocity, it will exhibit a distinct 'oscillatory' movement, during which the mean forward movement is accelerated.

(3) If now, without making any further alteration in the relative proportion of gas and air in the mixture, the experiment (2) be repeated, but instead of leaving the end of the tube nearest the sparking wires open a rubber stopper is inserted into it immediately before firing, it will be found that the flame will now traverse the whole length of the tube at a speed much faster than the observer's eyes can follow. The acceleration of the flame, which is really continuous from almost the start, is due to a series of compression waves reflected from the closed end of the tube.

(4) Finally, if, withdrawing the rubber stopper so as to have both ends of the tube open again, the relative proportion of air to gas in the mixture delivered to the tube is further increased, by suitable adjustment at the burner, until its composition approximates to that corresponding with the lower limit of inflammability (*i.e.* about 8 or 10 of gas to 92 or 90 of air), on subsequent ignition, a bluish-green flame will travel down the tube at about the same slow velocity as in the first experiment of the series, only now there is no reddish-brown tail to the flame; this is because, with excess of air present, the products issuing from the main body of the flame are no longer capable of interacting chemically as they cool down behind it.

CHAPTER XII *

THE INITIAL PHASES OF GASEOUS EXPLOSIONS (*Continued*)

Some Recent Experiments on Oxygen-Mixtures

During the course of an investigation primarily undertaken to test the validity of a new 'law of flame speeds' propounded by W. Payman and R. V. Wheeler in the year 1922—a subject which will be fully discussed in our next chapter—one of us, in conjunction with R. P. Fraser and D. A. Winter, discovered some new features of the initial flame movement through explosive mixtures which, when considered cumulatively, seem to throw doubt upon the hitherto prevalent suppositions (i) that, when an explosive mixture is ignited at the *open* end of a tube, an initial phase of 'uniform flame-movement' necessarily ensues, or (ii) that, if set up, its speed is chiefly inherent in the explosive mixture itself, 'environment' playing a subsidiary rôle.

It is proposed in this chapter to review some of the new evidence for the purpose of shewing how much the subject needs re-investigation, and how inadvisable it is for chemists to rest satisfied in any final sense with the position in which it was left by Mallard and Le Chatelier forty-five years ago. Indeed, we realise the necessity of dispelling some of the fog which in recent years has descended upon this part of the subject through too uncritical an acceptance of old positions which in science inevitably results in obscuration. For, so long as we consistently apply the true scientific method to such problems, there neither will, nor can, be any "abiding place"; on the contrary, we shall go on "from strength to strength," only as we by continual searchings "prove all things, holding fast to that which is good."

Up to now most of the existing data concerning flame speeds during the initial 'uniform movement,' after ignition of an explosive mixture at the *open* end of a tube, refer to mixtures of combustible gases with air in various proportions. Comparatively little is known concerning the behaviour of 'oxygen' mixtures in such circumstances. Mallard and Le Chatelier did indeed attempt, with doubtful success, to measure the initial speed of uniform flame propagation through various explosive hydrogen-oxygen mixtures when ignited near the *open* end of a 1 cm. glass tube, with the following results :

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* This and the two following chapters have been reproduced by permission of the Council, with slight alterations, from papers recently published by W. A. Bone and his collaborators in the *Proceedings of the Royal Society A*. 114 (1927), pp. 402 to 449.

Percentage Composition of Mixture.		Initial Flame Speed.
H_2	O_2	Cms. per sec.
33	67	1000
50	50	1700
77	23	1800
84	16	1300
89	11	800

They considered such speeds to be too high, however, for the true uniform movement, "*Car la propagation de la flamme a toujours été accompagnée des mouvements vibratoires.*"

The recent investigations in our laboratories at the Imperial College, London, have been concerned with the initial propagation of flame through undiluted explosive mixtures of oxygen with various proportions of hydrogen, ethylene or acetylene, respectively, many of which are very sensitive and fast-burning. For this purpose it was considered advisable to install special apparatus which will now be described.

The Methods employed for Measuring Flame Speeds

(*i*) *The Photographic Method.*

There can be no doubt that, whenever the actinic qualities of the flame permit, a photographic method on the lines employed by Mallard and Le Chatelier is preferable to any other, because it enables not only flame speeds to be measured with reasonable accuracy but also the whole flame movement to be studied visually. The problem was to devise an apparatus which would give good records of flame movements through such fast burning mixtures as we proposed to study, some of which were not highly actinic.

The apparatus employed, some details of which are shewn in Fig. 31, comprised a revolving metal drum *A*, six inches in diameter, fixed horizontally on its axis within a light-tight camera box *BB*, carrying a 2 mm. horizontal slit *C*, running the width of the drum, in front of which is a suitable wide-angle lens *L*. The drum could be revolved by means of a special shunt-wound constant speed electric motor *M*, through special gearings at any constant speed between 20 and 3000 r.p.m., the last named corresponding to a peripheral speed of 2400 cms. per second past the camera slit. The exact drum speed in any given experiment was registered by a Jaeger time-speedometer X, registering every half second, the reading being taken at the instant of firing.*

One of two lenses was employed in the camera according to circumstances, namely: (i) whenever the flame luminosity permitted, a Zeiss lens of 7 cms. focal length $f/1{\cdot}4$ focussed on fast bromide paper $4\frac{1}{2}$ inches wide, or (ii) a quartz lens of 6 cms. focal length $f/1{\cdot}8$ focussed on a film 2 inches wide of maximum sensitivity obtainable.

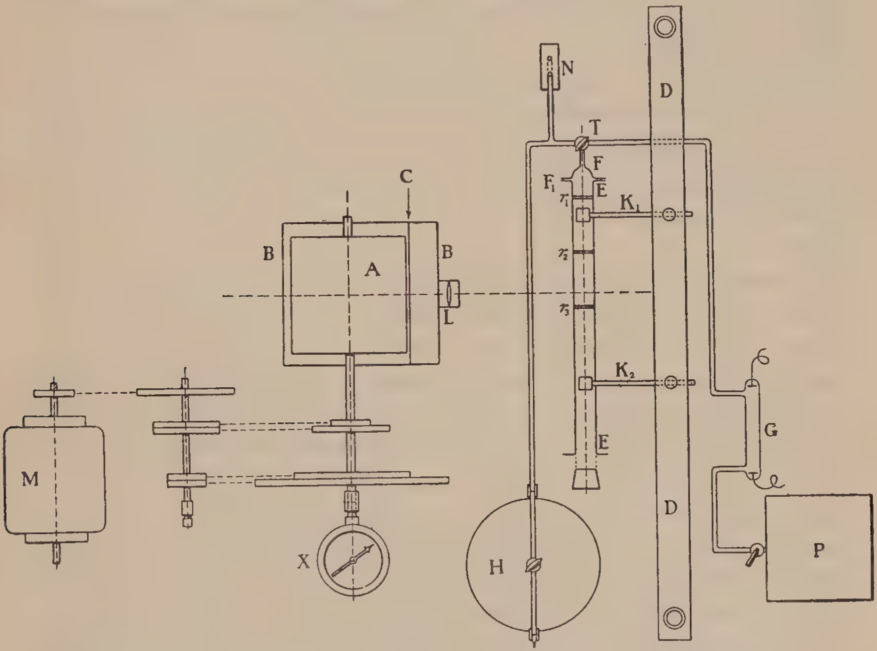

FIG. 31.—APPARATUS FOR MEASURING FLAME SPEEDS BY PHOTOGRAPHIC METHOD. (Bone, Fraser and Winter.)

Glass or quartz explosion tubes of 2·5 cms. internal diameter were used throughout the experiments, one and the same tube being employed throughout each series. In an experiment the tube EE was firmly clamped at K_1 and K_2 to a massive bridge DD erected over the table but independent of it so as to avoid the tube being affected by any slight camera vibration. Strips of black paper r_1, r_2 and r_3, serving as reference marks, were gummed on the tube at distances of 2, 12 and 22 cms. respectively from its flanged mouth F_1. This flanged mouth was closed by a movable piece F carrying a three-way tap T (2 mm. bore), one branch of which was connected by a glass tube through an 8 inch discharge tube G to a large capacity vacuum pump P, capable of evacuating the whole system down to $\frac{1}{10}$th mm. pressure within a minute. The other branch of T was connected through a T-piece to (a) the mercury manometer N

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* The accuracy of the speedometer was checked at the outset by a direct tuning-fork method.

and (*b*) the 10 litre mercury gas holder *H* containing the explosive mixture under investigation. The other end of the explosion tube *EE* was always closed by a rubber bung.

In making an experiment the explosion tube was first of all evacuated down to below $\frac{1}{10}$th mm., as indicated by the note of the pump and the appearance of the tube *G* under the discharge. The explosive mixture was then carefully admitted from the holder until the manometer *N* indicated a slight pressure (2 mm. or so) above that of the atmosphere. The image of the first 40 cms. of the explosion tube was focussed along the horizontal slit in the camera, and the drum was then set revolving at such a speed as would subsequently ensure a flame-graph angle somewhere between 25° and 40° with the horizontal. The explosive mixture in *EE* was then ignited by gently sliding off the flanged mouth-piece *F* and immediately applying a 2 cm. high coal-gas flame to the quiescent explosive mixture.

It should be noted that the arrangements were such that the first 20 cms. of the explosion tube (*i.e.* up to the second reference mark) was focussed in the centre of the field; the lens was always stopped down (often to *f* 6) as much as the luminosity of the flame permitted. The photographic paper or film as the case might be was subsequently developed and dried very evenly so as to avoid buckling or uneven contraction; and in finally making the angular measurements on the flame speed graph the image of the reference marks on the explosion tube gave a means of drawing a truly horizontal base line, and of measuring the ratio of length of object to image. From such angular measurements the true flame speed was calculated in each particular case by means of the usual formula.

It was found possible to apply the method to all the hydrocarbon-oxygen (or air) explosive mixtures, as well as to hydrogen-oxygen mixtures with initial flame speeds exceeding 1000 cms. per second approximately.

According to experience gained the probable experimental error in measuring flame speeds by this method may be put down as less than 2·5 per cent. We doubt whether any other method yet devised is capable of greater accuracy.

(ii) *The Electrical Method.*

The method employed for measuring flame speeds in cases of mixtures where the flames were insufficiently actinic to give good photographic records is based upon the fact that when a flame passes a gap in a high tension electric circuit too wide for the current to jump in an atmosphere of cold unburnt mixture, the ionisation produced permits of its doing so. By arranging a number of such gaps, each in an independent circuit, at known intervals along the inside of an explosion tube, together with supplementary narrow gaps outside the tube in series with each circuit, such outside gaps being suitably placed in the vicinity of a narrow revolving photographic film, means are obtained of measuring both the flame speed and the time during which the combustion products behind the flame remain ionised.

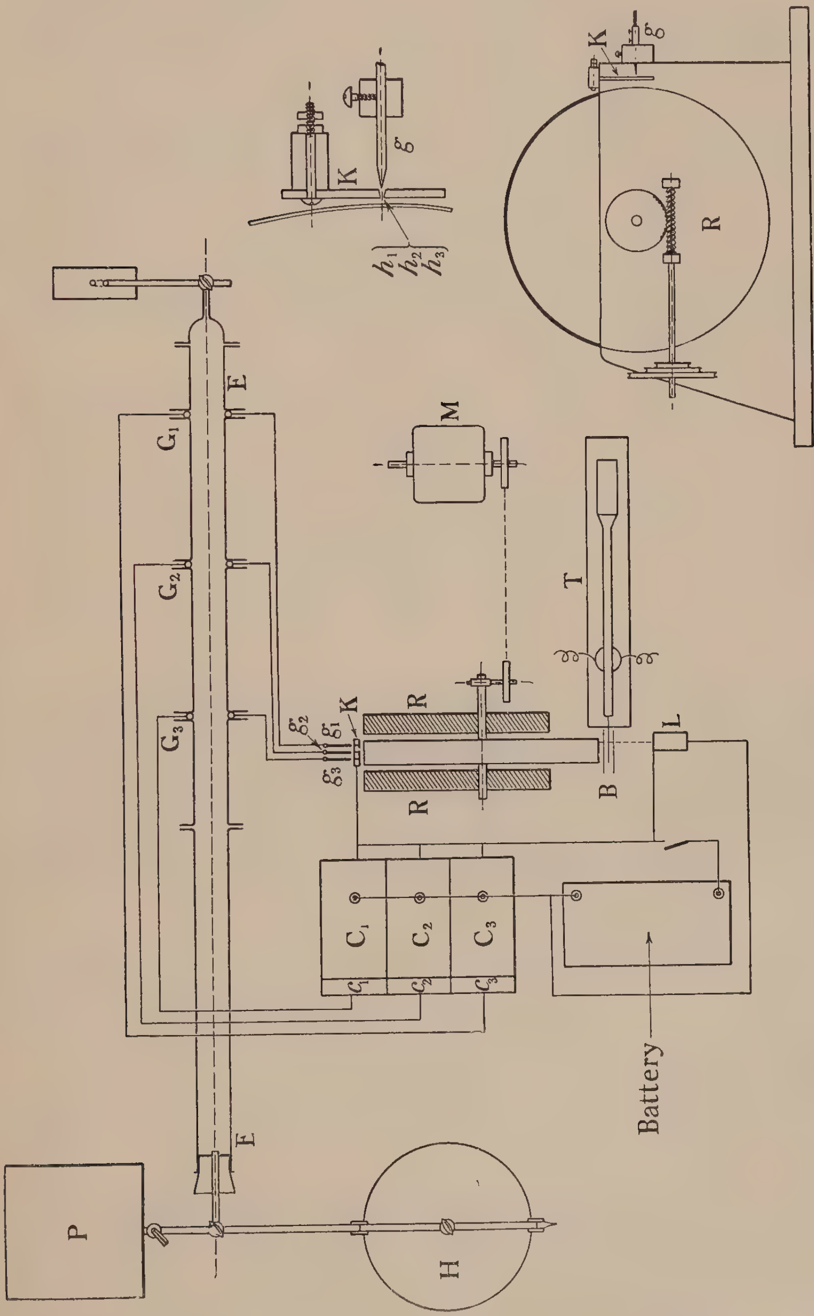

Fig. 32.—Apparatus for Measuring Flame Speeds by the Electrical Method. (Bone, Fraser and Winter.)

The apparatus, shewn in plan in Fig. 32, consisted principally of three parts, namely: (i) as a convenient source of high voltage, three induction coils C_1, C_2, C_3, with high speed make and break mechanisms; (ii) the explosion tube *EE* with gaps G_1, G_2, G_3; and (iii) a recorder *RR*.

The three similarly constructed induction coils were connected in parallel, each with its own tube spark gap *G*, and outside gap *g*, and the current to each primary was so adjusted as just to allow a sufficient discharge across the gaps *G* when the flame front reached them. The make and break mechanism employed gave 200 interruptions per second, but the insertion of a small capacity condenser (C_1, C_2 and C_3) in the secondary circuit of each coil, which remained charged during the $\frac{1}{200}$th of a second between successive interruptions, ensured that a spark would pass across a particular gap at the instant of the flame front meeting it, thus eliminating any errors which might arise through the make and break arrangement.

Into the glass explosion tube *EE* (internal diameter = 2·5 cms., and usually 120 to 150 cms. long) were fitted at regular intervals, 20 cms. apart, three pairs of brass ball electrodes, each ball $\frac{3}{16}$ths inch diameter forming the spark gaps G_1, G_2, G_3. The first of these was situated 7 cms. from the flanged mouthpiece of the tube. These electrodes were introduced through small side tubes sealed at right angles into the main tube; sealing-wax fillings were used to render all the side joints gas-tight, each carefully shaped on the inside so as to avoid any distortion of the circular section of the explosion tube.

The three supplementary outside spark gaps g_1, g_2, g_3 respectively, each in circuit with its corresponding inside gap G_1, G_2, G_3 respectively, were arranged in an ebonite mounting as three pointers within ·25 and 1 mm. of an earthed or negatively charged brass plate *K* through which three conical holes (h_1, h_2 and h_3, each $\frac{1}{100}$th inch diameter) were bored. By such means the sparks were photographed as minute dots upon a photographic film ($1\frac{1}{4}$ inches wide), fastened to the circumference of the revolving wheel (8 inches diameter) of the recorder *R*. Timing was effected by means of a tuning fork *T* interrupting a beam of light *L* through a hole in a plate *B* adjacent to the revolving film. The arrangements for evacuating the explosion tube by means of the oil pump *P*, filling it with the particular mixture under investigation, from the mercury gas holder *H*, and subsequently igniting by means of a 2 cm. high coal-gas flame at the open end, were similar to those employed in connection with the the photographic method, and therefore need not be detailed.

It was always necessary in measuring the speeds of the initial uniform movement in any given case to make sure that the time intervals occupied by the flames in travelling the successive distances between gaps G_1 to G_2, and G_2 to G_3, were substantially equal, for otherwise the uniformity of the movement might be doubtful. The substantial equality of the said two time intervals was regarded as a reasonable criterion of the uniform movement having existed at least throughout the 20 cm. distance between gaps G_1 and G_2.

Experience has shewn that this method may be used for measuring flame speeds certainly up to 300 cms., and in some cases even up to 600 cms. per second, with reasonable accuracy. And as it is principally in such low speed ranges that the photographic method may fail with mixtures where flames are feebly actinic, the electrical one is a most valuable adjunct to it.

Comparison of the Two Methods

On carefully comparing the two methods by using them simultaneously for speed determinations on a series of carbonic oxide-oxygen mixtures, in each case saturated with moisture at 12·5° C., the following results were obtained :

Percentage CO in CO/O_2 Mixture.	Speed in cms. per sec. of Initial Uniform Flame Movement as determined by	
	Photographic Method.	Electrical Method.
50·0	147	144
60·0	163	167
80·0	191	195
92·5	51	51

Also, in another simultaneous test with a 52·9 CH_4/47·1 O_2 mixture the photographic method gave 126 and the electrical method 122 cms. per second as the speed of initial uniform movement. Therefore it may be taken for granted that when used with the same mixture the two methods give results within about 2·5 per cent. of each other, *i.e.* within what we estimate to be the usual experimental error in such determinations.

Some General Observations upon the Initial Movement of Flame through Mixtures of Oxygen with Hydrogen, Ethylene, and Acetylene respectively

The experimental methods having been thoroughly tested, the next stage of the investigation was proceeded with, namely the determination of the speed of initial 'uniform' flame movement through stagnant mixtures of oxygen with hydrogen, ethylene, or acetylene, respectively, when ignited at 15°–18° C. and atmospheric pressure at the open end of a 2·5 cm. diameter tube (closed at the other end) by means of a 2 cm. high coal-gas flame. And it may be assumed that, unless otherwise stated, all the flame speeds given in this paper refer to such conditions. The experiments had to be carried out with exceptional care, because many of the mixtures concerned were so sensitive that it was only by scrupulous attention to details that reliable results could be obtained.

Needless to say every possible precaution was taken to ensure the purity of the various single gases (hydrogen, acetylene, ethylene and oxygen) used in making up the various experimental mixtures, special care being taken to reduce the amounts of adventitious nitrogen in them to the smallest dimensions ; it may be assumed that the amount of it present in the experimental mixtures never exceeded and was often less than one per cent.* The experimental mixtures were always made and stored under pressure in special 10 litre gas holders over mercury, and their compositions were always checked by chemical analysis. The windows of the laboratory in which all the operations, including the flame speed determinations, were carried out had dark blinds always kept drawn so as to exclude daylight. The room temperature remained between about 15° and 18° C. throughout the experiments.

Before detailing the flame-speed results, we think it desirable to say something about certain general features which seem to have an important bearing upon the proper interpretation of what has been termed hitherto " the initial uniform flame movement."

In the first place, with reference to the mixtures examined, it has been found that, whilst all those initially propagating flame under the stated conditions at speeds up to about 4000 cms. per second shewed a well-defined initial ' uniform movement,' the speed of which was substantially the same in successive determinations, those propagating at higher initial speeds behaved differently.

Thus, for example, with ethylene-oxygen or acetylene-oxygen mixtures initially propagating flame at speeds exceeding the aforesaid limit, no initial uniform movement at all was observable. On the contrary, the flame speed was continuously accelerated from the beginning, as though ignition had taken place near a closed instead of at the open end of the tube. Many photographic records shewing the striking contrast between the initial movements of flame through what may be termed ' slow ' and ' fast ' mixtures, respectively, of the same gas with oxygen were obtained during the research ; but for purposes of illustration we need only reproduce those shewn in Plate V, in which :

Fig. 33 = a typical record for a 50 C_2H_4/50 O_2 mixture initially propagating flame at the comparatively slow speed of 200 cms. per sec. The explosion tube in this case (as well as in Figs. 34 and 35) was 50 cms. long and 2·5 cms. internal diameter, ignition being at the open end. It will be observed that the initial speed remained perfectly uniform as far as the flame was photographed (15 cms.).

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* For convenience of recording the nitrogen content has been disregarded in the text ; hence readers will understand that, for example, when a 50C_2H_4/50O_2 mixture is referred to, it means that whereas the ethylene content was exactly as stated, the oxygen would include any small proportion of nitrogen which might be present.

PLATE V.

Fig. 33.—C_2H_4 50 per cent., O_2 50 per cent. Uniform Speed 200 cm./sec.

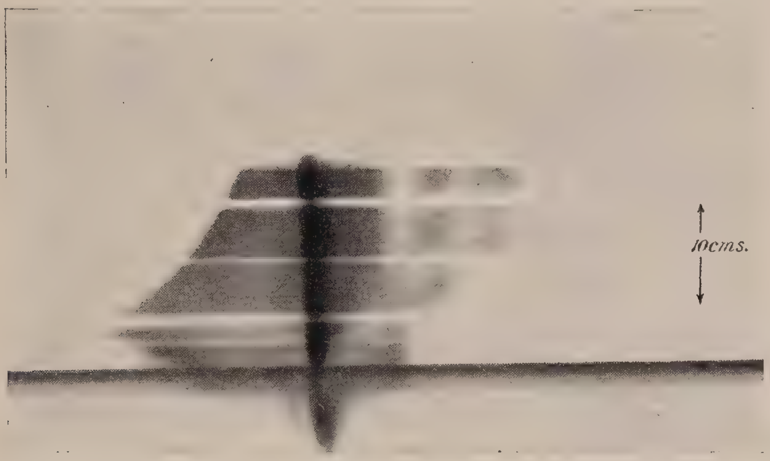


Fig. 34.—C_2H_4 20·6 per cent., O_2 79·5 per cent. Average Speed = 8320 cm./sec.

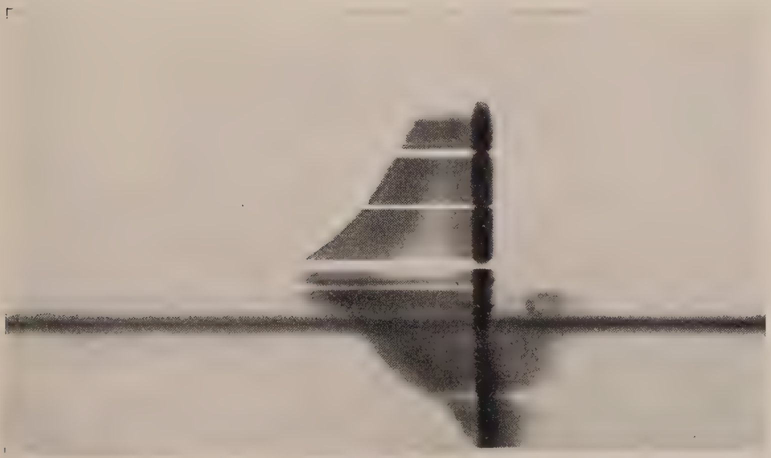


Fig. 35.—C_2H_4 35 per cent., O_2 65 per cent. Average Speed = 6250 cm./sec.

Initial Movements of Flames in Ethylene-Oxygen Mixtures.

Figs. 34 and 35 = typical records for 20 C_2H_4/80 O_2 and 35 C_2H_4/65 O_2 mixtures, respectively, initially propagating flame at speeds exceeding 4000 cms. per sec. In neither case was any uniform movement observable; on the contrary, the flame was continuously accelerated *ab initio*, detonation being set up near the far end of the tube (which was fitted with an extension of lead), as shewn by the 'retonation' wave thrown back through the still burning mixture in each case.

With hydrogen-oxygen mixtures a somewhat different, though equally well-marked, change took place when the aforesaid initial speed limit was exceeded. Instead of the initial flame movement losing its uniformity, as was the case with the acetylene- or ethylene-oxygen mixtures, it shewed a marked tendency to develop quite different uniform speeds in successive experiments.

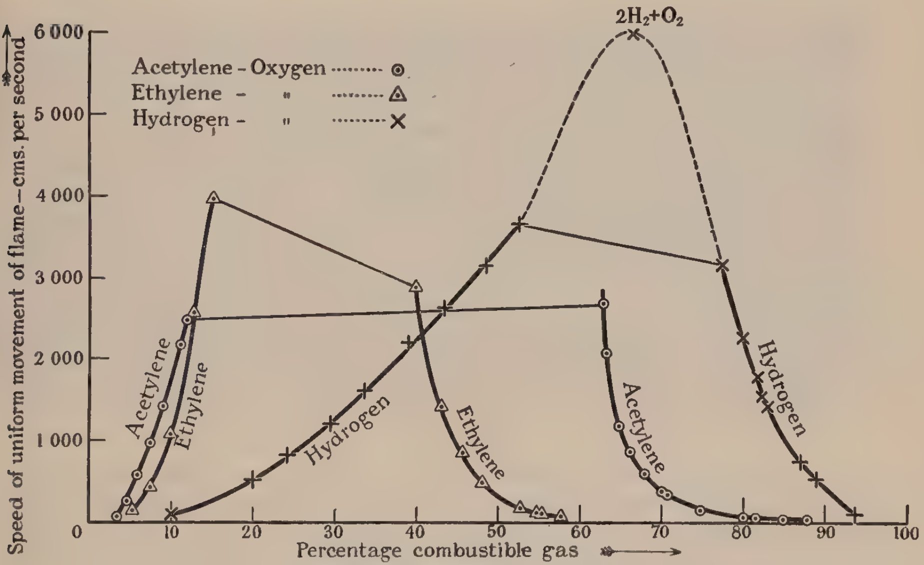


Fig. 36.—Speeds of 'Uniform Movement' in Hydrogen-, Ethylene- and Acetylene-Oxygen Mixtures. (Bone, Fraser and Winter.)

As a typical example of such happening we reproduce in Plate VI (Fig. 37) a print from a film upon which the results of three successive speed determinations with a 63·9 H_2/36·1O_2 mixture were photographically recorded, the drum speed remaining practically constant throughout the series. The peripheral film speeds were actually 1778, 1810, and 1812 cms. per sec. respectively in the three successive experiments. It will be seen that, although in each case the initial flame movement was quite uniform, three different angles (namely 41° 30′, 30° and 45°), corresponding with speeds of 5220, 3440 and 6000 cms. per second, respectively, were traced by the flames in successive determinations. Hence, it appears as though there are mixtures so highly sensitive as to be capable of initially propagating flame at quite different uniform speeds when ignited at the open end of a tube under, as near as could be judged, the same conditions.

It was found that all hydrogen-oxygen mixtures examined containing between about 55 and 75 per cent. of the combustible gas exhibited such a tendency. It seems difficult to say in any given case which of two or more observable speeds should be regarded as the normal one, although one speed (or one near to it) may be observed more frequently than others. Hence, the *dotted* part of the hydrogen-oxygen speed-curve shewn in Fig. 36 should be considered as provisional only.

A good deal of evidence has also been accumulated during the research, suggesting that, even with much slower-burning oxygen mixtures than those referred to in the preceding paragraphs, the speed of the initial uniform movement on ignition at the open end of a 2·5 cm. diameter tube, under the stated conditions, is not always quite so invariable as sometimes is supposed. Indeed, not infrequently in a series of successive speed determinations with one and the same mixture, under (so far as could be judged) the same experimental conditions, differences of the order of ten to twenty per cent. between the recorded speeds were observed, which certainly could not be attributed to any experimental error. Sometimes even, in one and the same experiment, after a certain run an initially quite uniform flame speed changed over abruptly and quite unaccountably to another.

Illustrations of such occasional happenings are shewn in the two photographic records reproduced in Plate VI, Figs. 38 and 39, in which :

Fig. 38 shews how, in two successive experiments, with a 9 C_2H_2/91 air mixture two different uniform speeds of 434 and 364 cms. per second respectively were recorded. The angles actually traced by the flame on the record were 18° 30′ and 15° 10′ respectively, although the film speed remained the same in the two experiments. Such a large difference clearly lies outside ‘ experimental error.’

Fig. 39 is the record (negative) obtained in an experiment with a 52·4 C_2H_4/47·6 O_2 mixture, which, on ignition under the stated conditions, initially propagated flame for a certain distance with a uniform speed of 89 cms. per sec., the angle initially traced by the flame on the record being 15° 30′; after travelling a certain distance, however, the flame abruptly changed to another uniform speed of 126 cms. per sec., now tracing an angle of 21° 30′ on the record.

We think it would be premature at this stage of the investigation to attempt any explanation of such facts ; at present our main business is to place them on record for future consideration. It is possible, however, that further investigation may shew that what has been found is not

PLATE VI.

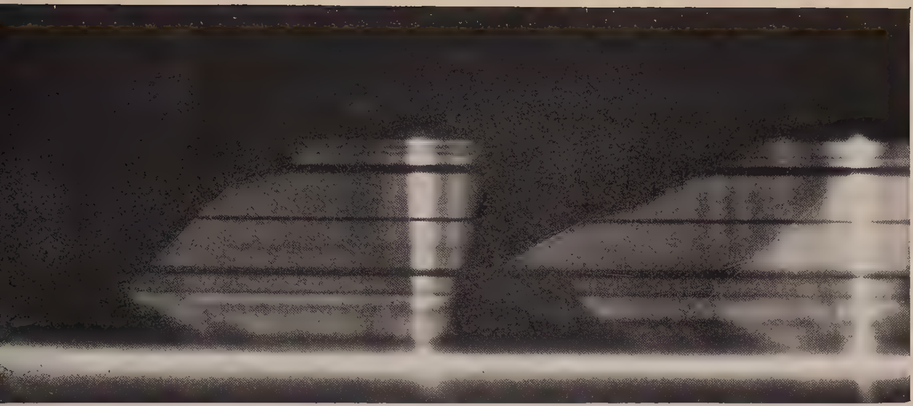


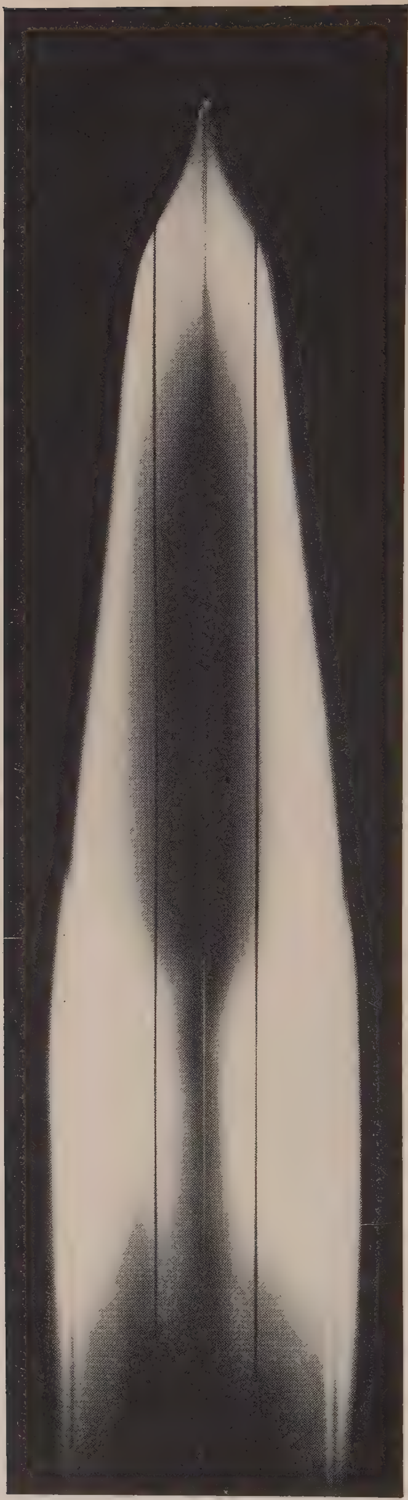
Fig. 37.—H_2 63·9 per cent., O_2 36·1 per cent. Angles, 41° 30′, 30° 45°.
Speeds, 5220, 3460, 6000.

Fig. 38.—C_2H_2 9 per cent., Air 91 per cent. Angles, 18° 30′, 15° 10′. Speeds, 434, 364.

Fig. 39.—C_2H_4 52·4 per cent., O_2 47·6 per cent. 1st Phase, 15° 30′ and 89.
2nd Phase, 21° 30′ and 126.

Initial "Uniform Movements" of Flames.

PLATE VII.



Flame Movements in a $2CO+O_2$ Mixture ignited at the centre of a closed Tube.

unconnected with some interesting observations recently made by C. Campbell and D. W. Woodhead * during their investigation of the ignition of gases by an explosion wave. For these authors have found that during the period immediately preceding detonation one or more separate regions of inflammation may appear in the unburnt gases in front of a flame, which, when photographed, appears serrated. Some of their unpublished photographs rather suggest this, and the matter is being studied further.

Such evidence as the foregoing has led us to doubt whether it is possible any longer rigidly to maintain *either* (i) that all quiescent explosive mixtures necessarily develop an initial *uniform* flame movement on ignition by means of a flame at the *open* end of a horizontal tube, *or* (ii) that even when a ‘ uniform movement ’ is initially set up in such circumstances its velocity is necessarily quite the same for the same tube diameter. In the latter case, doubtless, it *most frequently* happens that the observed initial uniform velocity for a given explosive mixture, and with one and the same tube diameter, will not differ very much from a certain mean value, which therefore may be regarded as having some significance relative *both* to the properties of the gaseous medium *and* to its environment. But it seems impossible to regard such *mean* uniform speed as a physical constant of the mixture in the same sense as we regard its ‘ rate of detonation.’

Lastly, it has been found possible under suitable conditions to have a slow ‘ uniform flame movement ’ developed in an explosive medium *after* a period of continuous acceleration, showing that such ‘ uniformity ’ is not necessarily restricted to the initial phase of flame movement. To illustrate this we reproduce in Plate VII a beautiful photographic record obtained on a film, which was rotated on a drum at a constant speed at right angles to the direction of the flame, when a mixture of carbonic oxide and oxygen in their combining proportions (dried by a three hours contact with pure redistilled phosphoric anhydride) was ignited at atmospheric temperature and pressure by a condenser discharge (3·75 m.f. at 1000 volts), passed between platinum electrodes fixed half-way along a horizontal glass explosion tube (length = 35 cms., internal diameter = 2 cms.) *closed at both ends.*

The flame started at the middle of the tube and travelled symmetrically along it in opposite directions towards each of the closed ends. It will be seen : (i) that after an initial period of accelerated flame velocity, extending about 5 cm. in each direction along the tube, a marked deceleration set in, culminating in a much slower ‘ uniform movement ’ which lasted until the flame had nearly reached the closed end of the tube ; (ii) that immediately afterwards the whole contents of the tube suddenly burst into an intense luminosity which continued for some time, as though the main combustion only occurred after the flame had reached the ends; and (iii) that, although the gaseous medium in the middle portion of the tube initially developed luminosity when the flame originally traversed it, soon afterwards it became dark again, and remained so until after the final burst of luminosity set in.

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* *Trans. Chem. Soc.* 1926, pp. 310–321.

We are thus led to conclude that, so far from a condition of 'slow uniform flame movement' *necessarily* arising when a quiescent explosive mixture is ignited at the *open* end of a tube, or from its being peculiar to such conditions, it may be set up in quite other circumstances. Also, that, besides the composition of the given mixture and the diameter of the tube in which it is ignited, other factors are concerned in determining the speed of such 'uniform flame movement' in any particular case.

Pending the results of further investigation we would refrain from expressing any decided opinion as to what governs such slow uniform movement in any given case; but at present we are inclined to attribute it to a certain balancing of the conditions as a whole rather than to any specific set of them. It seems reasonable to suppose that in any given circumstances its speed would depend *partly* on the chemical and thermal properties of the explosive mixture itself, and *partly* on the environment. Clearly it cannot be regarded as either necessarily caused by, or dependent upon, any particular mode of ignition or flame propagation; nor does its speed in any given case appear to be a physical constant of the mixture concerned.

Initial Uniform Flame Speeds of Hydrogen-Oxygen Mixtures

According to the experiments the 'range of inflammability' of hydrogen-oxygen mixtures for horizontal flame propagation in a 2·5 cm. diameter glass tube at room temperature and pressure lies between 10 and 94 per cent. hydrogen content approximately. With any given mixture containing either between 10 and 55, or between 75 and 94 per cent. of hydrogen, a fairly constant initial uniform flame speed was observed; but with a given mixture containing between about 55 and 75 per cent. of hydrogen, the initial speed, though always uniform, was apt to differ in successive experiments as already explained. The speeds actually observed with the different mixtures were as shewn on Table XXIX.

The foregoing results, together with those similarly obtained for acetylene-oxygen and ethylene-oxygen mixtures, are all plotted in the flame-speed curves shewn in Fig. 36. For convenience sake the two portions of the acetylene-oxygen and ethylene-oxygen curves, respectively, are in each case connected with a thin continuous straight line.

For reasons already explained the dotted upper portion of the hydrogen-oxygen curve should be considered as provisional; although probably for electrolytic gas a speed of about 6000 cm. per sec. may be accepted as fairly accurate.

So far as they go all the curves shew much the same general features as the lower portions of similar curves from the corresponding 'air' mixtures, except, of course, that the speed is generally much higher, and the range of inflammability much wider.

TABLE XXIX.—SPEEDS OF UNIFORM MOVEMENT * IN HYDROGEN-OXYGEN MIXTURES (BONE, FRASER AND WINTER)

Per cent. Hydrogen.		Speeds Determined. Cms. per sec.	Mean.
(1) Speeds both 'uniform' and fairly constant for each mixture.	10	64	64
	20	512	512
	24·2	880 ; 790 ; 866	845
	29·5	1250 ; 1150	1200
	33·8	1640 ; 1650 ; 1570	1620
	39·2	2200 ; 2240	2220
	48·5	3220 ; 3100	3150
	52·6	3670 ; 3690	3680
(2) Speeds, though always uniform in each experiment varied in successive experiments with each mixture.	63·9	5220 ; 6000 ; 3640	—
	69·7	5250 ; 6050 ; 6100	—
	71·25	5450 ; 3570	—
(3) Same as in (1).	77·5	3220 ; 3130	3170
	80·0	2290 ; 2270	2280
	81·6	1980 ; 1880 ; 1920	1930
	82·9	1470 ; 1410	1440
	87·5	730	730
	89·4	530	530
	93·5	76·5 ; 76·5	76·5
	94·4	*would not ignite*	—

Judging from these results, the 'lower limit' of inflammability of a combustible gas does not seem to be much affected by the substitution of air by oxygen in the explosive mixture ; but, as might be expected, the 'upper limit' is much higher with oxygen than with air. And, although the investigation was not primarily concerned with the exact determination of limits of inflammability, the results in this particular substantially confirm those published in 1920 by E. Terres (*vide* Chapter X. p. 100), allowing for the fact that, whereas his referred to 'downward,' the present ones refer to 'horizontal' flame propagation.

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* All the flame-speeds given in this table as well as in Fig. 36 refer to the initial uniform movement in a 2·5 cm. diameter horizontal glass tube, ignition having been effected by the gentle application of a 2 cm. high coal-gas flame at the open end, the other end being closed, the explosive mixture having been filled at 15°–18° C. and at atmospheric pressure.

CHAPTER XIII

AN EXAMINATION OF THE SUPPOSED LAW OF FLAME SPEEDS

In the year 1922 W. Payman and R. V. Wheeler published a paper entitled " The Combustion of Complex Gaseous Mixtures,"* in which it was stated " With each of the paraffin hydrocarbons the speed of the uniform movement of flame in its limit mixture with air is approximately the same under standard conditions of experiment," thus :

Table XXX.—Flame Speeds of ' Limit ' Hydrocarbon-Air Mixtures (Payman and Wheeler)

Paraffin Hydrocarbon.	Speed of Uniform Movement of Flame in horizontal glass tube 2·5 cm. diameter.	
	Lower Limit Mixture. Cms. per sec.	Higher Limit Mixture. Cms. per sec.
Methane - -	23·3	19·1
Ethane - -	18·1	19·7
Propane - -	20·8	20·3
Butane - -	20·1	20·3
Pentane - -	20·2	20·2

Moreover, after stating that " In general, if a limit mixture with air of one gas is mixed, in any proportions, with a limit mixture with air of another gas, the speed of propagation of flame in both mixtures being, as it is, approximately the same under the same conditions of experiment, the speed of propagation of flame in the resultant complex mixture (which is also a limit mixture) is unchanged," they proceeded to say that the same thing holds good for the propagation of flame " not only in limit mixtures, but in all mixtures of inflammable gases with air (or oxygen), provided that the mixtures of the individual gases are of the same type, all containing excess of oxygen, or all containing excess of combustible gas." And, finally, they promulgated a new " law of flame speeds," which ran as follows: "Given two or more mixtures of air or oxygen with different individual gases, in each of which the speed of propagation of flame is the same, all combinations of the mixtures of the same type * propagate flame at the same speeds, under the same conditions of experiment."

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* *Trans. Chem. Soc.* 121 (1922), pp. 363–379.

Since its original publication, they have continued to press this 'law' upon the attention of other workers in the field, using it as a basis for interpreting results from laboratories other than their own, even to the extent of claiming that it governs the division of oxygen between two combustible gases present in excess. Indeed, they contend that "So far as the propagation of flame is concerned, a mixture of a number of different combustible gases with air (for example) can be regarded as the summation of mixtures of each individual gas with air, the proportions of combustible gas and air in each being such that the speed of flame in it, if the mixture were burning alone, would be the same as in the complex mixture." Moreover, in the well-known case (investigated by one of us) of the explosion of mixtures of the type $CH_4+O_2+xH_2$, where the oxygen has the chance of combining with either of the two combustible gases, they claim that the methane gets the lion's share of it, not because of its greater affinity for oxygen but "because the methane-oxygen association that is required to yield the same speed of flame as the hydrogen-oxygen association is the richer in oxygen."

In a paper upon "The Interpretation of the Law of Speed," published by W. Payman in 1923,† two important passages occur which ought to be quoted here as shewing how he meant the 'law' to be regarded. The first ran as follows: "It will be seen that the law of speeds can be explained on the assumption that any addition of incombustible gas, inflammable gas, or oxygen to a mixture of inflammable gas and oxygen in combining proportions has a retarding effect upon the speed of the uniform movement of flame proportional to its specific heat" (*loc. cit.* p. 414), which seems to imply, what many will doubt, (i) that in the 'uniform movement' combustion is complete *in the flame front,* and (ii) *either* that 'dissociation' (not even that of carbon dioxide) has no influence at all upon the flame speed, *or* that the degree of it is unaffected by dilution with an inert gas or excess of one of the reactants.

The second passage implied a qualification, as follows: "The law of speeds as applied to the uniform movement during the propagation of flame can therefore be explained on the assumption that the variations in the speed of flame as determined under standard conditions with mixtures of different compositions depends on the rate of reaction between the inflammable gases and oxygen in the flame front. The law of speeds would hold exactly if this rate of reaction was dependent solely on the temperature, so that excess of either inflammable gas, oxygen, or of incombustible gas could be regarded as behaving simply as diluting gas, lowering the reaction temperature but taking no part in the reaction. The fact that the rate of reaction must also depend on the concentrations of the reacting gases results in small divergencies from the law when the oxygen is in deficit. The correction necessary to allow for this cannot be correctly estimated, but the general effect of this factor is to make the speeds of the uniform movement of flame in complex mixtures rather slower than the speeds calculated from the law of speeds" (*loc. cit.* p. 420). We are thus led to expect incalculable 'small divergencies' when oxygen is in deficit, which tend to make the flame speeds 'rather slower' than the 'law' would require, a vague sort of qualification, capable of being variously interpreted according to each individual's idea of what margin is allowable as a 'small divergence' from a supposed natural law without impugning its validity.

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* *i.e.* "all containing excess of oxygen or all containing excess of combustible gas."

† *Trans. Chem. Soc.* 123 (1923), pp. 412–420.

In a paper which Payman and Wheeler contributed to the discussion on "Explosive Reactions in Gaseous Media," held in London on 14th June, 1926, under the auspices of the Faraday Society,* they emphasised the operation of their supposed 'law,' claiming it to be applicable to *all* conditions of flame propagation; for they said: "There is a considerable amount of evidence available that the relative speeds of the uniform movement of flame obtained under the specified experimental conditions are directly proportional to the speeds under other conditions, except during the detonation wave" (*loc. cit.* p. 305).† Also, they claimed "that the law of flame speeds applies to the rate of development of pressure in mixtures of complex gas mixtures with air." The last-named statement seems to involve another questionable rule laid down and applied by them in 1923, namely that, in gaseous explosions generally, "the time taken for pressure within a spherical vessel to attain its maximum (ignition being in the centre) . . . coincides with the time taken for flame to reach the boundary of the vessel; except with very slowly moving flames." ‡

The basis of the experimental test to which the supposed 'law' has been subjected—in continuation of the researches described in the previous chapter—is one which the authors of it themselves have supplied. For in their paper at the Faraday Society they repeated that their 'law' states (i) "that if a complex mixture is made by blending a number of mixtures of air with simple combustible gases all of which have the same speed of uniform movement of flame, then this complex mixture will have the same speed of flame provided that all the mixtures are of the same type, all containing excess of oxygen or all containing excess of inflammable gas," and, again, that (ii) " an important deduction from the law of speeds is that during the propagation of flame in a complex mixture of combustible gas and air mixtures of the type we have just considered (all with the same speed of uniform movement of flame), the combustion can be regarded as involving the simultaneous but independent burning of a number of simple mixtures of the individual gases with air, in which the proportions of inflammable gas and air are such that each mixture, if burning alone, would propagate flame with the same speed as does the complex mixture." They also reported having found experimentally that complex mixtures of methane, hydrogen and air, containing insufficient oxygen for complete combustion, obey the law. As will be shewn, however, in the concluding portion of this chapter, such experience has not been confirmed.

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* *Trans. Faraday Soc.* xxii. (1926), pp. 301–306.

† *Trans. Chem. Soc.* 123 (1923), p. 1257.

‡ In the course of the discussion they said, however, that "the statement that the Law of Speeds is not applicable to the rates of detonation in gaseous mixtures is incorrect."

It may be observed that up to now Payman and Wheeler have chiefly relied on experimental evidence in support of their ' law ' derived from the study of comparatively slow-burning complex gas-air mixtures, when the ' diluent ' (if it can properly be so called) may exercise a considerable influence. Thus, in proof of the ' law ' they shewed experimentally in 1922 (1) that (*A*), a 7·35 methane/92·65 air, and (*B*), a 1·98 pentane/98·02 air-mixture—each of which, on ignition at the open end of a 2·5 cm. diameter horizontal glass tube, initially propagated flame at a uniform speed of 40 cms. per sec.—could be blended in any proportions without altering the initial flame speed, and (2) that the same holds good for (*A*), a 11·0 methane 89·0 air, and (*B*), 3·54 pentane/96·46 air mixtures, both of which initially propagate flame, in said circumstances, with an initial speed of 60 cm. per sec. We think, however, that such evidence lacks cogency as regards proving a general law, because (i) the mixtures in question are all comparatively *slow* burning, (ii) they would all contain somewhere between about 70 and 82 per cent. of ' diluent ' (chiefly nitrogen), (iii) the two combustible gases concerned are homologous hydrocarbons, presumably with similar modes of combustion, (iv) in the case of (i), where oxygen was always in excess, presumably the flame speed would be chiefly governed by some relationship between the heat of combustion and the heat capacity of the products, which calculation shews would not alter very much in the various blendings, and (v) in the case of (ii), in which the two primary mixtures both contained excess of combustible gas, the percentage of oxygen in the various blended mixtures between $100A/0B$ and $0A/100B$ would not vary by more than from 18·7 to 20·7 per cent., which in our opinion would be far too little for a really valid test of the matter.

It has always seemed to us necessary that before any final opinion can be expressed concerning its validity the ' law ' should be thoroughly tested out in regard to complex ' oxygen ' mixtures, containing two combustible gases as dissimilar as are (say) hydrocarbons and hydrogen in their modes of burning. Accordingly, experiments of this character were undertaken with results as recorded herein, which seem to us to be decisive against it.

We will now proceed to submit the evidence as succinctly as possible, leaving the reader to form his own judgment upon it.

Experimental

In all that follows it should be understood:

(i) That the various experimental mixtures were all made up in gasholders over mercury from highly purified gases, and that their compositions were all checked by analysis.

(ii) That, for convenience sake, they are usually recorded as x gas/y oxygen mixtures, x being the exact percentage of combustible gas present, and y that of the oxygen *plus* (usually less than 1 per cent. of) adventitious nitrogen.

(iii) That, *unless otherwise expressly stated*, all 'flame speeds' recorded refer to the initial uniform movement through the quiescent mixtures in question at about 15° to 18° C. and atmospheric pressure, on ignition by the gentle application of a 2 cm. high coal-gas flame at the *open* end of a horizontal glass tube of uniform bore, 2·5 cm. in diameter. For brevity such will always be referred to as 'the standard conditions.'

(iv) That the letters (P.M.) or (E.M.) in brackets are used to indicate which of the two experimental methods (photographic or electrical) described in Chapter XII. hereof was employed for the flame speed measurement in any particular case.

Evidence derived from the Explosion of (*a*) $C_2H_4+H_2+O_2$ *and* (*b*) $C_2H_2+2H_2+O_2$ *Mixtures*

When the law was first promulgated it called to mind two significant experiments, made more than twenty years ago by W. A. Bone and J. Drugman during their researches upon the explosive combustion of hydrocarbons, to which we would now particularly direct attention.* It was found that when *either* an ethylene-hydrogen-oxygen mixture of the composition $C_2H_4+H_2+O_2$ *or* an acetylene-hydrogen-oxygen mixture of the composition $C_2H_2+2H_2+O_2$ is exploded in a glass bulb (60 c.c. capacity) not a trace of carbon separates, nor does any steam condense on cooling. Indeed, with the $C_2H_2+2H_2+O_2$ mixture no appreciable steam is produced at all, and with the $C_2H_4+H_2+O_2$ mixture the amount formed is insufficient to saturate the cold products if at the outset they are practically dry: The results of two such typical experiments are shewn in Table XXXI., where:

$$\left.\begin{array}{l} p_1=\text{initial pressure of the dry combustible mixtures when fired} \\ p_2=\text{final pressure of the dry products} \end{array}\right\}\text{both at } 15^\circ\text{ C.}$$

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* *Trans. Chem. Soc.* 89 (1906), pp. 669–671.

TABLE XXXI.—BONE AND DRUGMAN'S EXPERIMENTS

Original Mixture.		$C_2H_4+H_2+O_2$			$C_2H_2+2H_2+O_2$.		
	p_1	503 mm.			534 mm.		
	p_2	750 mm.			653 mm.		
	p_2/p_1	1·49			1·22		
Per cent. Composition of Gaseous Products.	CO_2	0·35			0·2		
	CO	39·60			39·8		
	$C_2H_2+C_2H_4$	1·25			*nil*		
	CH_4	3·65			0·2		
	H_2	55·15			59·8		
Units of		C	H	O	C	H	O
in	Original mixture	341	505	168	267	400	133
in	Gaseous products	346	478	151	262	394	131
Difference		—	27	17	Negligible		

These remarkable experiments, which were shewn at the Royal Institution in 1908, and have since been repeated many times, seemed incompatible with the supposed 'law' except on the very unlikely supposition that even the *slowest* burning ethylene-oxygen or acetylene-oxygen mixture propagates flame faster than the *fastest* burning hydrogen-oxygen mixture. A glance at the flame-speed curves shewn in Chapter XII. Fig. 36 hereof will shew how untenable is any such supposition.

It is worth while considering the matter a little further, however, and in a somewhat different way. According to the supposed 'law,' whenever either of the two complex mixtures referred to is exploded, the oxygen (being in defect) must be divided between the two combustible gases concerned in such proportions as would give rise to *two* primary (hydrocarbon-oxygen and hydrogen-oxygen) mixtures propagating flame with the same speed as does the original complex mixture itself. But such prediction is falsified by the event, as the following typical experimental results obtained with the $C_2H_4+H_2+O_2$ mixtures shew.

(*a*) *The* $C_2H_4+H_2+O_2$ *Mixture*

(i) First of all a moist mixture containing

$$C_2H_4=34{\cdot}0,\ H_2=33{\cdot}6,\ \text{and}\ O_2=32{\cdot}4\ \text{per cent.}$$

was carefully made up in a holder over mercury, and, after its composition had been determined by analysis, three successive measurements were made (P.M.) of its flame speed when ignited under the standard conditions. The photographic records shewed that in all cases the initial flame movement had been quite uniform, and the observed speeds of it were :

Observed speeds : 83·0, 77·2, and 75·2 cm. per sec.

Mean=78·5 cm. per sec.

(ii) From the flame-speed curves shewn in Chapter XII. (Fig. 36 *q.v.*) it was seen that a speed of 78·5 cms. per sec. should be given by a primary 55·5 C_2H_4/44·5 O_2 mixture. Accordingly this was carefully made up in a holder over mercury, and four successive measurements of its initial uniform flame speeds were subsequently made (P.M.) under the standard conditions, as follows :

Observed speeds : 70·4, 75·0, 76·4, and 78·0 cms. per sec.

Mean=75 cm. per sec.

Within the limits of experimental error this substantially confirmed the speeds predicted from our curve.

(iii) By calculation it was deduced that the only hydrogen-oxygen mixture which could be added in any proportion to the aforesaid 55·5 C_2H_4/44·5 O_2 mixture, in order to produce the aforesaid complex $C_2H_4+H_2+O_2$ mixture, would be a 86·75 H_2/13·25 O_2 mixture. But, according to the hydrogen-oxygen flame speed curve shewn in Chapter XII. (Fig. 36) hereof, the initial flame speed of such a mixture, on ignition under stated conditions, would be as high as 790 cms. per sec., or about ten times that required by the supposed law.

(iv) Moreover, the said hydrogen-oxygen flame speed curve predicted that an initial speed of 75 cms. per sec. should be given by a 93·45 H_2/6·55 O_2 mixture. Accordingly, this was made up over mercury and its flame speed determined (E.M.) on ignition under the standard conditions, with the following results :

Observed speeds : 76·5, 76·5, 77·4 cms. per sec.

Mean=76·8 cms. per sec.

Thus confirming again the so predicted speed. But, by no possible blending of this mixture with the aforesaid 55·5 C_2H_4/45·5 O_2 mixture, referred to in (ii) could the original 34·0 C_2H_4 +33·6 H_2 +32·4 O_2 complex-mixtures referred to in (i) be obtained.

From the foregoing it would appear that the behaviour of a $C_2H_4+H_2+O_2$ mixture does not harmonise with the supposed 'law.'

(*b*) *The* $C_2H_2+2H_2+O_2$ *Mixture*

Further evidence as to the behaviour of this complex-mixture will be submitted further on in this chapter.

Evidence derived from Blending Tests

Undoubtedly the simplest and most direct test of the validity or otherwise of the ‘ law ’ is that propounded by its authors, namely : “ That if a complex mixture is made by blending a number of mixtures of air with simple combustible gases all of which have the same speed of uniform movement of flame, then this complex mixture will have the same speed of flame provided that all the mixtures are of the same type, all containing excess of oxygen or all containing excess of inflammable gas.” Accordingly, as will hereinafter be outlined, such a ‘ blending test ’ has been applied to a number of complex ‘ oxygen ’-mixtures (both *fast* and *slow*), as well as to one complex ‘ air ’-mixture. In all the experiments one of the two primary mixtures employed has always been a hydrogen-oxygen (-air) mixture, and the other a hydrocarbon-oxygen (-air) mixture, the hydrocarbon used being either acetylene, ethylene or methane.

The Experimental Procedure

It should be explained that the experimental procedure adopted in carrying out such blending tests was briefly somewhat as follows :

(i) At the commencement of each series of experiments, with the help of the flame-speed curves shewn in Chapter XII. (Fig. 36) hereof, about 10 litres of each of two *primary* mixtures were made up in a gas-holder over mercury, namely : (*A*) of a hydrocarbon-oxygen (-air) mixture, and (*B*) of a hydrogen-oxygen (-air) mixture respectively, each of the same type (*i.e.* each containing either excess of combustible gas or excess of air), and each having as nearly as possible the same initial speed of uniform flame movement when ignited under the standard conditions.

(ii) Successive measurements were then made of the initial flame speeds of each of the said two primary mixtures, and if the *mean* results agreed within (say) 5 per cent. the mixtures were deemed suitable for the subsequent ‘ blending tests.’ The exact composition of each primary mixture was then ascertained by careful analysis, and until the subsequent ‘ blending tests ’ were completed each was kept stored over mercury at a pressure greater than that of the atmosphere, so as to minimise any chance inleakage of air.

(iii) The desired proportions of each of the said two primary mixtures *A* and *B* were next separately measured out, as accurately as possible, over mercury in a 1000 c.c. graduated cylindrical gas-burette, and successively transferred under pressure to another gas-holder over mercury, where they were thoroughly blended, so as to produce the desired ‘ complex mixture ’ *C*, whose exact composition was afterwards determined by analysis. As a rule, a series of such complex mixtures was so made up by blending different proportions of the two primary mixtures (75*A*/25*B*, 50*A*/50*B*, 25*A*/75*B*, etc.) for subsequent examination. The usual order of such blending was, first of all, 50/50, and afterwards (as far as possible) alternately on either side of it.

(iv) Successive flame-speed measurements under the standard conditions were then made with each said complex-mixture so prepared, using, in most cases, and whenever possible, the photographic method.

(v) Finally, after all the said flame-speed measurements had been completed those of each of the two primary mixtures *A* and *B* were repeated, so as to ensure that they had undergone no alteration during the time covered by all the foregoing operations.

Purity of the Gases

Throughout all the experiments the utmost care was taken to ensure the purity of all the gases employed, including their practical freedom from adventitious nitrogen. Each of the hydrocarbons (acetylene, ethylene or methane) used was purified not only by chemical methods but also finally by liquefaction and fractionation of the liquid. The hydrogen used was prepared by the action of pure dilute sulphuric acid upon Mond's 'Crescent' electrolytic zinc (99·98 per cent. purity), and was subsequently washed by passage through a train of 'worms' containing a hot alkaline solution of potassium permanganate. The oxygen used was prepared by gently heating recrystallised potassium permanganate, and was washed by passage through a strong solution of caustic potash. Special attention was paid to minimise 'adventitious' nitrogen, both in preparing the original gases and in subsequently making up the various experimental mixtures from them. Indeed, the arrangement of all the 'generating' and 'mixing' apparatus was such as easily allowed both the complete evacuation of all vessels and connections before or during each preparation, etc.; and, in the mixing operations, the complete filling beforehand of all vessels and connections with mercury. By such means we often succeeded in reducing the 'adventitious' nitrogen in the experimental mixtures to less than 0·5 per cent.; and in nearly all other cases to within 1 per cent.; and it never exceeded 1·5 per cent. The accuracy of the mixing arrangements employed may be judged by the always close correspondence (as shewn in the tabulated experimental results) between the 'found' and 'calculated' composition of the various complex-mixtures employed.

Tabulation of Results

In most cases the verdict of the various blending tests upon the matter at issue can be seen at a glance from the tabulated results, which in each case shew :

(i) The composition of each of the two primary mixtures *A* and *B*, respectively, employed.

(ii) The observed 'flame-speeds' under the standard conditions for each primary mixture *A* and *B* respectively, both *before* and *after* the blending tests.

(iii) The proportions in which the two primary mixtures *A* and *B* were blended to produce each of the complex mixtures *C* examined.

(iv) The observed flame speeds, on ignition under the standard conditions, for each complex mixture *C* examined.

(v) The composition of each complex mixture examined.

(*a*) *Complex Acetylene-Hydrogen-Oxygen Mixtures*

It was ascertained by reference to the flame-speed curves shewn in Chapter XII. (Fig. 36), supplemented by actual trial, that two primary mixtures (*A*) $64{\cdot}5\ C_2H_2/35{\cdot}5\ O_2$ and (*B*) $83\ H_2/17\ O_2$, each containing excess of combustible gas, should give the same initial uniform flame speed when ignited under the standard conditions. And, as it was calculated that, on blending them in the proportions $38{\cdot}3A/61{\cdot}7B$, a complex mixture very nearly of the composition $C_2H_2+2H_2+O_2$ would result, it was decided to employ them in these tests. They both propagated flame under the standard conditions at a high initial speed, which was found to be uniform for a sufficient distance to enable reliable speed measurements to be made. The mixtures were, however, rather, 'sensitive'; so, to make things reasonably sure, two separate series of blending tests were carried out at different times with fresh mixtures in each case.

It will be seen that in neither series did the experimental results which are set forth in Tables XXXII. and XXXIII. agree with the 'law.' For, in the first series, the effect of blending the two primary mixtures *A* and *B* was, in most cases, to depress their original flame speeds by from about 1400 to about 1200 cms. per sec., or by nearly 15 per cent. In the second series the speed-depression was, in some cases, even greater, namely, from about 1380 to about 1050 cms. per sec., or by nearly 25 per cent. Because of the sensitiveness of these mixtures we do not stress any particular figure, but the general implication of the results as a whole is, we think, unmistakable.

In two respects, however, the divergencies of these mixtures from the 'law' differed from that of any of the other complex hydrocarbon-hydrogen-oxygen mixtures studied, in that (i) it was much less marked, and (ii) apparently reached a maximum at a region somewhere between 50*A*/50*B* and 38·3*A*/61·7*B*, instead of progressively increasing with the proportion of *B* in the various blendings.

TABLE XXXII.—FLAME SPEEDS OF COMPLEX ACETYLENE-HYDROGEN-OXYGEN MIXTURES (SERIES I.) (BONE, FRASER AND WINTER)

Percentage composition of the primary mixtures *A* and *B*				
	A	C_2H_2 64·4	O_2 35·4	N_2 0·2
	B	H_2 83·1	O_2 15·4	N_2 1·5

Observed flame speeds (cms. per sec.) for *A* and *B* *before* and *after* the blending experiments		Before		After	Mean
	A	1435	1420	1380	1410
	B	1390	1380	1410	1390

Proportions of *A* and *B* blended to form *C*.		Observed flame speeds for the complex mixture *C*.		Percentage composition of *C*. (i) found, and (ii) calculated.			
A	*B*	Cms. per sec.			C_2H_4	H_2	O_2 and N_2
75	25	1170		(i)	48·0	21·0	31·0
				(ii)	48·3	20·8	30·9
50	50	1220	1190	(i)	32·4	41·3	26·3
				(ii)	32·2	41·6	26·2
38·3	61·7	1190	1200	(i)	24·8	50·7	24·5
				(ii)	24·75	51·25	24·0
25	75	1220	1240	(i)	16·2	61·8	22·0
				(ii)	16·1	62·3	21·6
12·5	87·5	1375		(i)	7·9	72·9	19·2
				(ii)	8·05	72·7	19·25

N.B.—All flame-speeds measured photographically.

This last-named peculiarity seemed to synchronise with an interesting feature observed in the corresponding photographic records, some of which (from the first series of experiments) are reproduced in Plate VIII. (Figs. 40 to 43). It will be seen that, whilst both the 100*A*/0*B* and the 50*A*/50*B* mixtures (the same also held good for the 38·3*A*/61·7*B* mixture) exhibited a well-defined ‘ uniform ’ flame movement, which, in course of time, was succeeded by a peculiar kind of vibratory period, in the case of the 25*A*/75*B* mixture the flame movement was not quite uniform from the first, and in the case of the 12·5 *A*/87·5*B* mixture never at all. The peripheral speed of the drum to which the photographic films were

PLATE VIII.

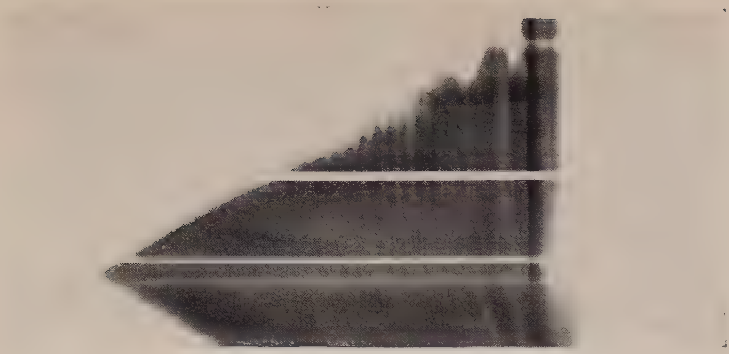


Fig. 40.—100A, 0B. Angle, 30°. Speed, 1435.

Fig. 41.—50A, 50B. Angle, 25° 48′. Speed, 1190.

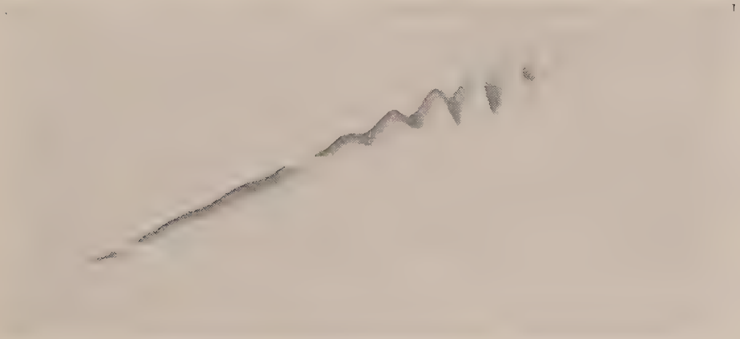
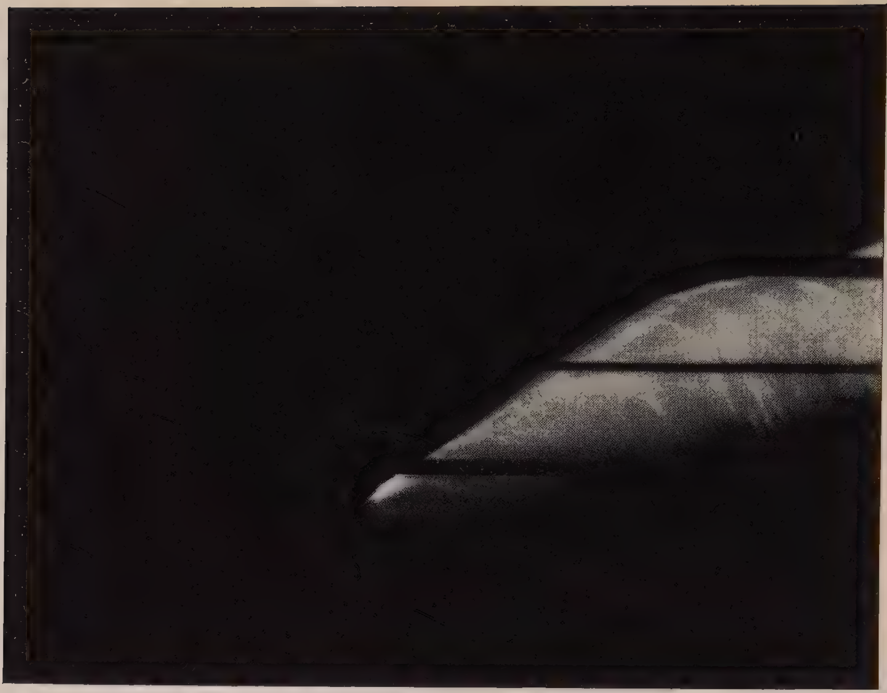


Fig. 42.—25A, 75B. Angle, 26° 30′. Speed, 1240.

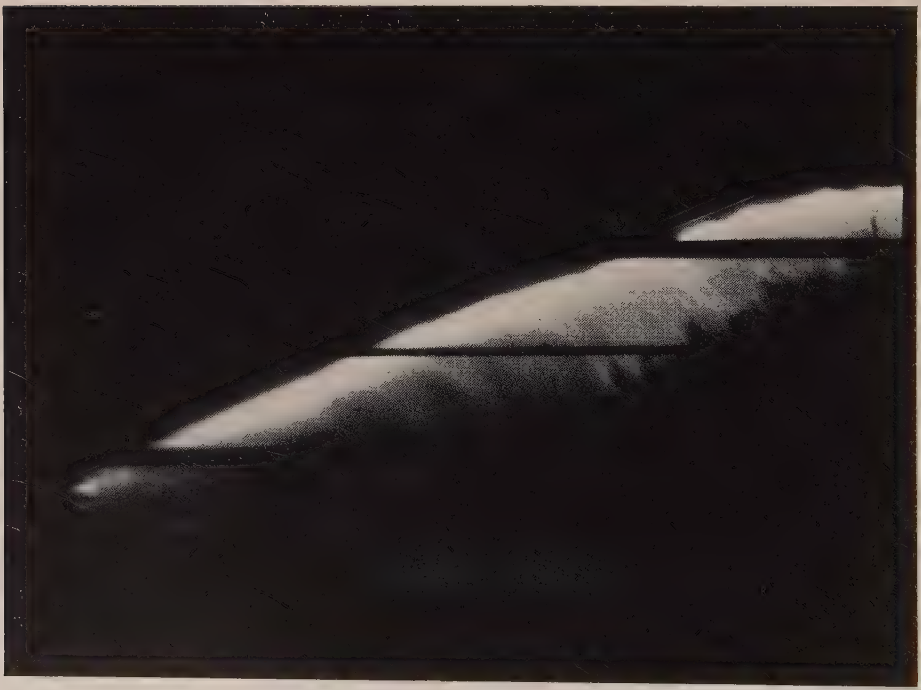
Fig. 43.—12·5A, 87·5B. Angle, variable. Speed uncertain.

Initial Movements of Flames in Acetylene-Hydrogen-Oxygen Mixtures.



A.—C_2H_2 19 per cent. $(2H_2+O_2)$ 81 per cent.

Fig. 44.



B.—C_2H_2 22 per cent. $(2H_2+O_2)$ 78 per cent.

Fig. 45.

Initial Movements of Flames in Acetylene-Electrolytic Gas Mixtures.

attached being constant (within 1 per cent.) throughout the series, visual evidence of the divergencies of these mixtures from the ‘law’ is offered by the very different angles traced by the flame during the initial uniform movement in the case of the 100*A*/0*B* and the 50*A*/50*B* mixtures, namely 30° in the first and only 25° 48′ in the second case. In the 0*A*/100*B* photographic record, which shewed a quite uniform initial flame movement, the angle traced was 29° 48′.

TABLE XXXIII.—FLAME SPEEDS OF COMPLEX ACETYLENE-HYDROGEN-OXYGEN MIXTURES (SERIES II.) (BONE, FRASER AND WINTER)

Percentage composition of the primary mixtures *A* and *B*	*A*	C_2H_2 64·6	O_2 35·2	N_2 0·2
	B	H_2 83·0	O_2 15·5	N_2 1·5
Observed flame speeds (cms. per sec.)				Mean
	A	1380	1330	1355
	B	1440	1380	1410

Proportions of *A* and *B* blended to form *C*.		Observed flame speeds for the complex mixture *C*.		Percentage composition of the complex mixture *C* (calculated.)		
A	*B*	Cms. per sec.		C_2H_2	H_2	O_2
90	10	1315		58·15	8·30	33·55
75	25	1200	1170	51·45	20·75	27·80
50	50	1070	1045	34·3	41·5	24·2
38·3	61·7	1060	1020	—	—	—
25	75	1235	1190	17·15	62·2	20·65
12·5	87·5	1280		8·05	72·5	19·45

N.B.—All flame speeds measured photographically.

Incidentally it may be mentioned that, in another connection, we have recently discovered that successive additions of acetylene to electrolytic gas, so as to produce a series of complex mixtures $xC_2H_2/(100-x)(2H_2+O_2)$, have a peculiar disturbing influence upon the uniform character of the initial flame movement. Such influence reached a maximum when $x=$about 20, after which it subsided and eventually disappeared, so that with $x=30$ it was hardly appreciable. This feature is well brought out in the two beautiful photographic records (P.M.) reproduced in Plate IX., of which *A* (Fig. 44) was given by a 19 $C_2H_2/81(2H_2+O_2)$, and *B* (Fig. 45) by a 22 $C_2H_2/78(2H_2+O_2)$ mixture, when ignited under the standard conditions. Attention is directed to the non-uniformity of the flame movement, more marked in *A* than in *B*, as well as to the 'feathery' character of the pictures, the cause of which we desire to reserve for further investigation. The mean 'flame speed' in *A* was nearly 4000 cms. per sec. and in *B* between 2200 and 2500 cms. per sec. It seems possible that the peculiarities referred to in this and the two preceding paragraphs may be in some way connected with the endothermic character of acetylene; but, however that may be, we think that in all probability they may be referred to some common cause.

(*b*) *Complex Ethylene-Hydrogen-Oxygen Mixtures*

Complex ethylene-hydrogen-oxygen mixtures seemed well-suited for testing the validity of the supposed 'law' because of the heat of formation of the hydrocarbon being only −2·7 K.C.U. per gram-molecule, as compared with −47·8 for acetylene and +21·7 for methane. That used in our experiment was generated by Newth's method, and finally liquefied, and the liquid fractionated, the first and last portions being rejected. Analyses shewed the final product to be very pure and practically nitrogen-free.

In order to make the subsequent blending tests as complete as possible three different series were carried out, namely, two in which the primary mixtures employed both contained excess of combustible gas, and the third in which they both contained excess of oxygen. The primary mixtures used in the tests, and their 'flame speeds,' when ignited under the standard conditions, were as follows:

TABLE XXXIV.—FLAME SPEEDS OF PRIMARY ETHYLENE-OXYGEN AND HYDROGEN-OXYGEN MIXTURES (BONE, FRASER AND WINTER)

Series.	Composition of the Primary Mixture.		Flame Speeds. Cms. per sec.	
	A C_2H_4/O_2	*B* H_2/O_2	*A*	*B*
I. - -	55·45/44·55	93·45/6·55	75	77
II. - -	49·9/50·1	92·5/7·5	177	181
III. - -	12·35/87·65	38·7/61·3	2195	2190

In most cases the photographic method was employed for the flame speed measurements; and in all cases, without exception, throughout the three series the initial flame movement was quite uniform. The results of the tests, which speak for themselves, are shewn in Tables XXXV., XXXVI. and XXXVII.

It will be seen that in each of Series I. and II., when the primary mixtures all contained excess of combustible gas, *successive increases in* *the proportion of the B mixture used in the blendings always lowered progressively the flame speed of the resulting complex mixtures, until in each case a point was reached when the latter no longer propagated flame.* It may also be noted that, in a letter to *Nature* on 8th January, 1927 (Vol. **119,** p. 51)

TABLE XXXV.—FLAME SPEEDS OF COMPLEX ETHYLENE-HYDROGEN-OXYGEN MIXTURES (SERIES I.) (BONE, FRASER AND WINTER)

Percentage composition of the primary mixtures *A* and *B*				
	A	C_2H_4 55·45	O_2 44·35	N_2 0·2
	B	H_2 93·45	O_2 6·45	N_2 0·1

Observed flame speeds (cms. per sec.) for *A* and *B* *before* and *after* the blending experiments.		Before		After	Mean
	A	70·4 76·4	75·0 78·0	75·7	75·4
	B	76·5 77·4	76·5	80·0	78·0

Proportions of *A* and *B* blended to form *C*.		Observed flame speeds for the complex mixture *C*.		Percentage composition of *C*, (i) found, and (ii) calculated.			
A	*B*	Cms. per sec.			C_2H_4	H_2	O_2+N_2
90	10	68·4	65·5	(i)	50·1	9·3	40·6
				(ii)	49·9	9·35	40·55
75	25	47·5	50·0	(i)	41·5	23·5	35·0
				(ii)	41·58	23·36	35·06
50	50	43·1	42·9	(i)	27·6	46·8	25·6
				(ii)	27·7	46·7	25·6
35	65	25·7		(i)	19·25	62·15	18·6
				(ii)	19·4	61·8	18·8
25	75	22·3	22·3	(i)	13·6	71·1	15·3
				(ii)	13·85	71·1	15·05
15	85	Did not fire.					
5	95						
1	99						

upon the "Supposed Law of Flame Speeds," A. G. White, after saying that it "must break down when one of the combustible gases in a complex mixture interferes with the burning of another," stated that, "By mixing suitable carbon disulphide-air and (say) ether-air mixtures having the same speed of flame, mixtures can be obtained which refuse to propagate flame." In Series I., when the two primary mixtures were both slow burning, being not far removed from the 'higher limit,' this point was reached at 20*A*/80*B*. In Series II., when the primary mixtures were faster burning, a greater proportion of *B* was required in the blending to render the resulting mixture non-inflammable. In this connection

TABLE XXXVI.—FLAME SPEEDS OF COMPLEX ETHYLENE-HYDROGEN-OXYGEN MIXTURES (SERIES II.) (BONE, FRASER AND WINTER)

Percentage composition of the primary mixtures *A* and *B*				
	A	C_2H_4 49·9	O_2 49·9	N_2 0·2
	B	H_2 92·5	O_2 7·4	N_2 0·1

Observed flame speeds (cms. per sec.) for *A* and *B* *before* and *after* the blending experiments.		Before		After		Mean
	A	177·7	177·3	186·0	187·0	180·8
		176·2				
	B	182·0	180·0	178·0	186·0	181·5

Proportions of *A* and *B* blended to form *C*.		Observed flame speeds for the complex mixture *C*.		Percentage composition of *C*.		
A	*B*	Cms. per sec.		C_2H_4	H_2	O_2+N_2
90	10	141·0		44·9	9·3	45·8
80	20	119·7	135·5	39·9	18·5	41·6
47·5	52·5	89·3		23·7	48·6	27·7
20	80	60·5	43·0	10·0	74·0	16·0
15	85	37·0	37·4	7·5	78·7	13·8
1·5 1 0·5	98·5 99 99·5	Did not fire.				

it is interesting to recall how, during his classical researches upon flame, Sir H. Davy found that both ethylene and methane (but especially the former) have a much greater power of rendering electrolytic gas non-inflammable than has a corresponding excess of either hydrogen or oxygen, a circumstance which cannot possibly be ascribed to the known difference in their molecular heat capacities. Thus, for instance, he found that whereas 1 volume of electrolytic gas could be rendered non-inflammable

PLATE X.

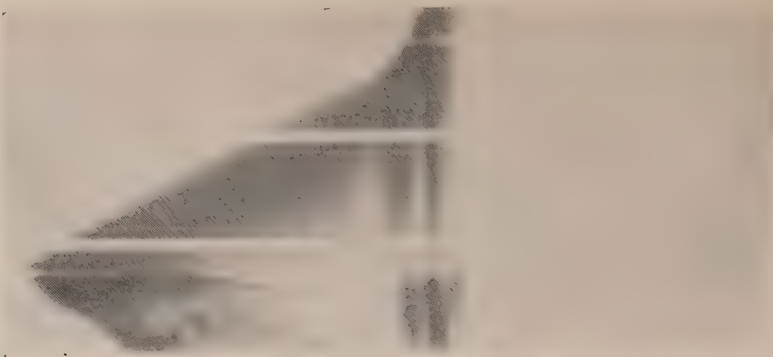


Fig. 46.—100A, 0B. Angle, 28° 10′. Speed, 177·7.

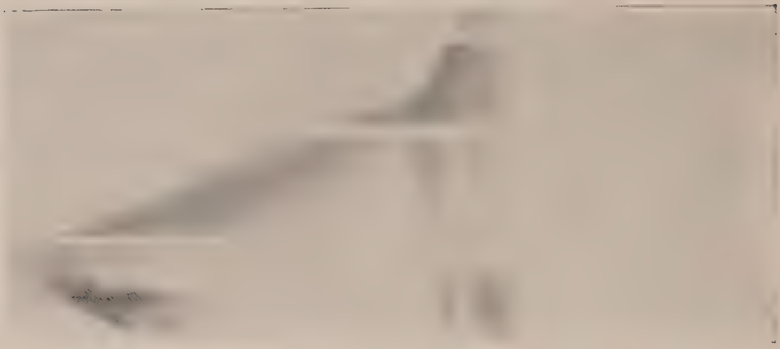


Fig. 47.—90A, 10B. Angle, 22° 40′. Speed, 141.

Fig. 48.—80A, 20B. Angle, 17° 20′. Speed, 119·7.

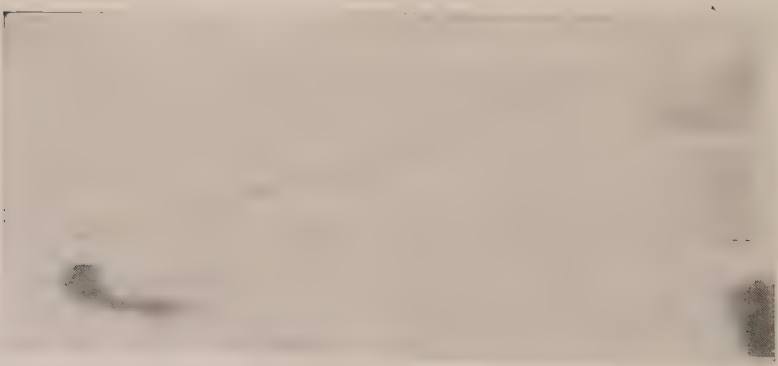


Fig. 49.—40A, 60B. Angle, 15°. Speed, 82·1.

Initial Movements of Flames in Ethylene-Hydrogen-Oxygen Mixtures.

(by "a strong spark from a Leyden Jar") by dilution with either about 0·5 volumes of olefiant gas, or about 1·0 of marsh gas only, no less than 8 volumes of hydrogen or 9 of oxygen were required.

In carrying out Series I. and II. the eye could easily detect, without the aid of any photographic records, the progressive slowing up of the flame speeds as the proportion of *B* in the various blendings was increased. But, in order to obtain permanent visual evidence of the fact, as well as of the 'uniformity' of the initial flame movements, in Series II. the peripheral speed of the drum to which the photographic paper was attached in each case, was kept constant (within 3·5 per cent.) throughout the series. In Plate X (Figs. 46 to 49) are reproduced four of the actual photographic records, so that the reader may see for himself how the angle traced by the flame with the horizontal (and consequently the flame speed) diminished as the proportion of *B* in the blendings increased; the angles, and corresponding flame speeds, were as shewn on p. 150.

TABLE XXXVII.—FLAME SPEEDS OF COMPLEX ETHYLENE-HYDROGEN-OXYGEN MIXTURES (SERIES III.) (BONE, FRASER AND WINTER)

Percentage composition of the primary mixtures *A* and *B*	*A*	C_2H_4 12·35	O_2 87·55	N_2 0·1	
	B	H_2 38·7	O_2 61·2	N_2 0·1	
Observed flame speeds (cms. per sec.) *before* and *after* the blending experiments		Before		After	Mean
	A	2130 2240	2212 2200	2185	2190
	B	2180	2200	—	2190

Proportions of *A* and *B* blended to form *C*.		Observed flame speeds for the complex mixture *C*.		Percentage composition of *C*, (i) found, and (ii) calculated.			
A	*B*	Cms. per sec.			C_2H_4	H_2	O_2+N_2
75	25	3050	3090	(i)	9·3	10·05	80·65
				(ii)	9·25	9·65	81·1
50	50	(1410) 2900	(1450) 2900	(i)	6·15	19·3	74·55
		3270		(ii)	6·2	19·35	74·45
25	75	3660	3000	(i)	3·05	29·2	67·75
				(ii)	3·1	29·05	67·85

In Series III., where the two primary mixtures *A* and *B* both contained excess of oxygen, and were very fast-burning and sensitive, it was found that, with blendings in the proportion 75*A*/25*B*, 50*A*/50*B* and 25*A*/75*B*, respectively, whereas in the first and last cases the observed flame speeds were all between 40 and 70 per cent. higher than those of the two primary mixtures, in the case of the 50/50 blendings two quite different initial flame speeds were observed in five determinations; thus in *three* of them the speed was between 32 and 50 per cent. *higher*, but in the other *two* it was about 30 per cent. *lower*, than the speed of either of the two primary mixtures blended. In this connection the reader is referred to what is said in Chapter XII. hereof about the possibility of variability in initial flame speed in one and the same mixture, when it is very sensitive. In none of the speeds measured, however, were the requirements of the supposed 'law' fulfilled.

TABLE XXXVIII.—SHEWING DETAILS OF PHOTOGRAPHIC RECORDS REPRODUCED IN PLATE X

Record.	Proportion of Primary Mixture.		Drum Speed.	Angle.	Calculated Flame Speed. Cms. per sec.
	A	B			
Fig. 46	100	0	118·8	28° 10′	178
„ 47	90	10	120·6	22° 40′	141
„ 48	80	20	116·4	17° 20′	120
„ 49	40	60	118·5	15° 0′	82

(c) *Complex Methane-Hydrogen-Oxygen Mixtures*

The case of these mixtures is of particular interest because of Payman and Wheeler's claim that when a complex mixture of methane, hydrogen, and oxygen, the last-named being in deficit, is inflamed, the resulting distribution of the oxygen between the two combustible gases is governed by their 'law.' If, however, as the results prove, such a mixture does not obey the law, the claim in question cannot be sustained.

In making the experiments very pure gases were used in making up two primary mixtures, the amounts of adventitious nitrogen present in either of them being well below 0·5 per cent. The following two primary mixtures, each containing excess of combustible gas and propagating flame with an initial uniform speed of about 115 cms. per sec., were selected for the blending test, namely:

Mixture.	Composition.	Mean Flame Speed. Cms. per sec.
A	$53{\cdot}2\ CH_4/46{\cdot}8\ O_2$	115
B	$92{\cdot}9\ H_2/7{\cdot}1\ O_2$	113

The electrical method (E.M.) was used throughout for the flame speed determination. From the results of the blending tests, which are shewn in Table XXXIX., it will be seen that, as in the case of the corresponding ethylene-hydrogen-oxygen mixture, *successive increases in the proportion of mixture B used in the blendings progressively lowered the flame speed of the resulting complex mixture, until a point was reached when the latter no longer propagated flame.* Thus, with a 25*A*/75*B* complex mixture, the original flame speeds of *A* and *B* were already more than halved, and a 10*A*/90*B* mixture would not propagate flame under the stated experimental conditions.

TABLE XXXIX.—FLAME SPEEDS OF COMPLEX METHANE-HYDROGEN-OXYGEN MIXTURES (BONE, FRASER AND WINTER)

Percentage composition of the primary mixtures *A* and *B*				
	A	CH_4 53·2	O_2 46·5	N_2 0·3
	B	H_2 92·9	O_2 7·0	N_2 0·1

Observed flame speeds (cms. per sec.) for *A* and *B* *before* and *after* the blending experiments		Before		After		Mean
	A	110	117	117·5		115·5
	B	112	113	113	116	113·25
		112	110			

Proportions of *A* and *B* blended to form *C*.		Observed flame speeds for the complex mixture *C*.	Percentage composition of *C*, (i) found, and (ii) calculated.			
A	*B*	Cms. per sec.		CH_4	H_2	O_2+N_2
72·5	27·5	94·0	(i)	38·1	25·5	36·4
			(ii)	38·6	25·5	35·9
45	55	72·7	(i)	24·3	51·2	24·5
			(ii)	23·95	51·1	24·95
25	75	50·0	(i)	13·4	70·3	16·3
			(ii)	13·3	69·7	17·0
10 2·5	90 97·5	Did not fire.				

(*d*) *Complex Methane-Hydrogen-Air Mixtures*

In the paper which they contributed to the Faraday Society discussion (*loc. cit.* p. 305), Payman and Wheeler said: "Two mixtures, one of methane and the other of hydrogen, with air, having the same speed of flame and containing insufficient oxygen for complete combustion, contain widely different proportions of inflammable gas and oxygen. During the propagation of flame in a complex mixture of methane, hydrogen and air, made by blending these two mixtures, the combustion of the methane-air mixture is as though it were alone or as though the hydrogen-air mixture that dilutes it were a further quantity of the methane-air mixture. That is to say, during its burning in the complex mixture the methane behaved as though it were still associated with the greater proportion of the oxygen, and combines with that greater proportion. This we have shewn experimentally " (and there was given a reference to their original paper, *J.C.S.* 1922 (**121**), p. 363).

On looking at that paper, however, not more than one actual blending test could be found in it, giving flame speeds, with such methane-air and hydrogen-air mixtures, namely : in which (as is said—*loc. cit.* pp. 371 to 376) two primary mixtures, (*A*) a 12·5 CH_4/87·5 air, and (*B*) a 70·2H_2/29·8 air mixture, both having the same flame speed of 30 cms. per sec. in a 2·5 cm. diameter tube, were blended so as to give a complex mixture (*C*) containing :

$$CH_4=10{\cdot}25\ H_2=9{\cdot}99\ O_2=16{\cdot}16 \text{ and } N_2=63{\cdot}6 \text{ per cent.}$$

without altering the flame speed. We would point out, however, that (i) a simple calculation will shew that the complex mixture in question could not have been produced by the blending in any proportions of the two aforesaid primary mixtures, unless some inleakage occurred during the process, and (ii) that a speed of only 30 cms. per sec. for a 70·2 H_2/29·8 air mixture in a tube 2·5 cms. in diameter seems difficult to reconcile with a previous statement by Payman * that, " it was not found possible to determine accurately the speed of the uniform movement of flame in the upper limit mixture of hydrogen-air in a tube 2·5 cms. in diameter. A mixture containing 71·4 per cent. of hydrogen was found to be the richest which would propagate flame under the experimental conditions . . . but its speed . . . was found to be approximately 50 cms. per sec." A speed has recently been found by the electrical method of 50 cms. per sec. for a 72·6 H_2/27·4 air mixture.

The number of possible primary methane-air and hydrogen-air mixtures fulfilling the required conditions, *i.e.* each containing excess of combustible, and both propagating flame with the same initial uniform speed, being limited to a small range, our choice of these was necessarily restricted. Eventually, after one or two trials the following two primary mixtures were selected for a series of blending tests, each of which fulfilled the required conditions :

	Flame Speed. Cms. per sec.
Mixture *A*, 11·05 CH_4/88·95 air †	64·5
Mixture *B*, 71·9 H_2/28·1 air †	64·1

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[*] *Trans. Chem. Soc.* **115** (1919), p. 1456.

[†] As the amount of adventitious nitrogen in the combustible gas used in making these mixtures was less than 1·0 per cent., the composition of the air added was not seriously altered thereby.

TABLE XL.—FLAME SPEEDS OF COMPLEX METHANE-HYDROGEN-AIR MIXTURES (BONE, FRASER AND WINTER)

Percentage composition of the primary mixtures *A* and *B*	*A*	CH_4 11·05	O_2 18·3	N_2 70·65
	B	H_2 71·9	O_2 5·75	N_2 22·35

Observed flame speeds (cms. per sec.) for *A* and *B* *before* and *after* the blending experiments.		Before		After		Mean
	A	65·0 65·0	64·0	64·0		64·5
	B	63·0 64·5	63·0 61·5	64·7	64·5	64·1

Proportions of *A* and *B* blended to give *C*.		Observed flame speeds of complex mixtures *C*.	Percentage composition of *C*, (i) found, and (ii) calculated.				
A	*B*	Cms. per sec.		CH_4	H_2	O_2	N_2
90	10	61·3	(i)	10·25	6·9	16·6	66·25
			(ii)	9·96	7·19	16·57	66·28
75	25	38·5	(i)	8·45	17·8	14·75	59·0
			(ii)	8·31	17·98	14·74	58·97
62·5	37·5	32·5	(i)	6·6	26·9	13·3	53·2
			(ii)	6·91	26·95	13·23	52·91
50	50	26·6 26·2	(i)	5·9	35·75	11·65	46·7
			(ii)	5·54	35·95	11·95	46·56
37·5	62·5	23·7	(i)	3·8	44·7	10·3	41·2
			(ii)	4·15	44·9	10·45	40·5
25	75	Did not fire.	(i)	2·8	53·6	8·7	34·9
			(ii)	2·77	53·92	8·9	34·41

N.B.—Electrical method used throughout.

The electrical method (E.M.) was used throughout for the flame speed determinations. The results of the blending tests, which are shewn in Table XL., again shewed that, as in the cases of the corresponding ethylene-hydrogen-oxygen, and methane-hydrogen-oxygen mixtures, *successive increases in the proportion of B used in the 'blendings' progressively slowed up the initial uniform flame speed of the resulting complex mixture until a point was reached that it no longer propagated flame at all.* In this case such point was nearly reached with the 37·5*A*/62·5*B* complex mixture, and had been passed with the 25*A*/75*B* complex mixture.

In a final experiment, in which were blended equal volumes of the following two primary mixtures, namely:

	Flame Speed. Cms. per sec.
A, 11·5 CH_4/88·5 air	52
B, 72·6 H_2/27·4 air	51

the resulting 50*A*/50*B* complex mixture propagated flame quite easily at a uniform speed of 21 cms. per sec. A 35*A*/65*B* blend, however, refused to propagate flame at all.

Summary

The results of most of the various 'blending-tests,' which have comprised a fairly wide range of complex hydrocarbon-hydrogen-oxygen (or air) mixtures, some of them initially propagating flame rather slowly, and others quite rapidly, are summed up in the accompanying diagram (Fig. 50). The hydrocarbons used have comprised the strongly endothermic acetylene, ethylene—which is only slightly endothermic—and the exothermic methane. Most of the complex mixtures examined have contained excess of combustible gases, but in one series they contained excess of oxygen. In none of the series have the requirements of the supposed 'law' been fulfilled, as a glance at the diagram will shew,

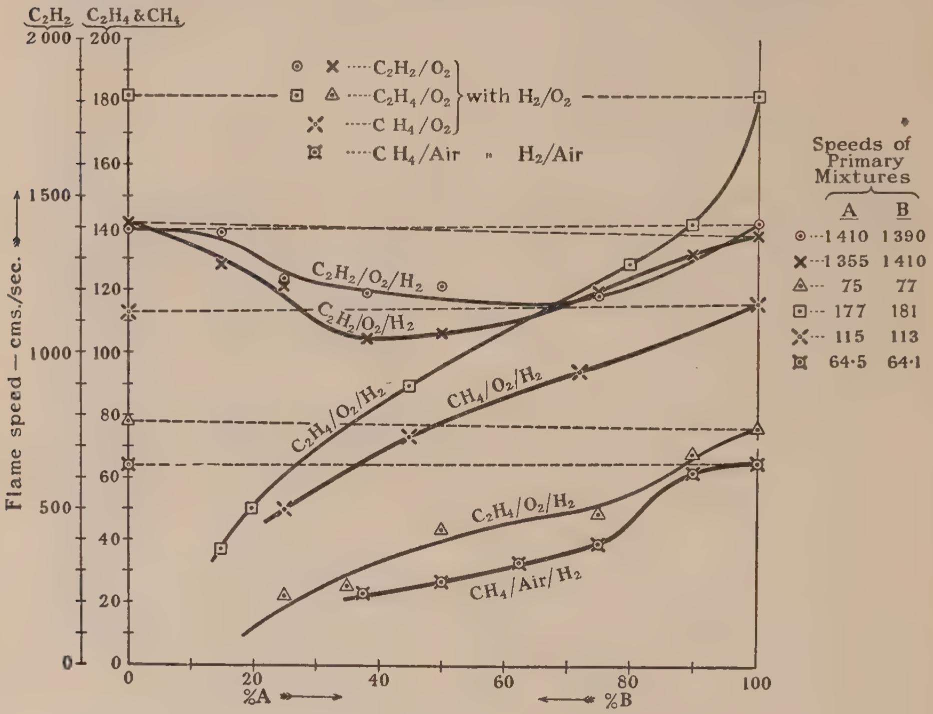

FIG. 50.

because, had the ‘ law ’ been obeyed, all the lines in it would have been horizontal straight lines.

Moreover, in all the cases which have been examined of complex ethylene-hydrogen-oxygen and methane-hydrogen-oxygen (or air) mixtures with oxygen in defect, it was found that the effect of progressively increasing the proportion of the primary hydrogen-oxygen (air) mixture *B* in the various blendings in any particular series was progressively to lower the observed flame speed, until a point was reached when the resulting complex mixture refused to propagate flame at all under the stated experimental conditions. Such a result is not surprising when the effect of progressively increasing the proportion of the hydrogen-oxygen (air) mixture in the various blendings upon the oxygen content of the resulting complex mixture in any particular series is considered, but it seems fatal to the supposed ‘ law.’

It therefore follows that whatever measure of truth there may be in Payman and Wheeler’s conclusions in regard to particular instances, they are not generally applicable to gaseous explosions, and therefore cannot be vested with the authority of a natural law.

CHAPTER XIV

RECENT EXPERIMENTS ON THE INITIAL PHASES OF THE EXPLOSION OF AN EQUIMOLECULAR METHANE-OXYGEN MIXTURE

As part of the general investigation of the initial stages of gaseous explosions carried out at the Imperial College, London, a study has recently been made photographically by W. A. Bone, R. P. Fraser, and F. Witt of the behaviour of an equimolecular methane-oxygen mixture when ignited by sparks of varying intensities passed between electrodes fixed halfway along a horizontal glass tube (35 to 50 cms. long × 2 to 2·5 cms. diameter), both ends of which were *closed* in one series of experiments but *open* in another. A few supplementary experiments were also made under other spark-igniting conditions and a number of interesting photographs were obtained.

The evidence of the experiments lies so much in the photographs themselves that little need be said about them beyond indicating the precise conditions under which they were obtained. It is left to each reader to study them for himself, because, while their main features will be obvious to all, their interpretation leaves room for discussion, which it is hoped their publication will provoke.

To us they suggest such possibilities as (*a*) the occurrence, under ordinary sparking conditions, of what seems to be much like a definite ‘ induction period ’ as a preliminary to the actual combustion ; (*b*) an initial propagation through the medium of a ‘ ghost-like flame ’ condition involving only a very partial combination of the gases ; and (*c*) the main combustion following later as the result of the superposing of a compression wave, or, the like, upon a system which during the phase (*b*) has already become highly sensitive to chemical changes.

Experimental

In all the experiments an equimolecular mixture of methane and oxygen made up from highly purified gases was employed. The chemical reactions involved in the explosive combustion of such a mixture are known to be as follows: namely, (i) the primary interaction of methane and oxygen producing a mixture of carbonic oxide, hydrogen and steam, probably as a result of the thermal decomposition of the incipiently formed dihydroxy methane, thus:

$$CH_4+O_2=[CH_2(OH)_2]=CO+H_2+H_2O;$$

and (ii) secondary interactions in the reversible system

$$CO+OH_2\rightleftharpoons CO_2+H_2.$$

The end products before condensation of steam would consist of a mixture of the oxides of carbon, hydrogen and steam in somewhat the following proportions:

$$CO_2=5{\cdot}0,\ CO=28{\cdot}25,\ H_2=38{\cdot}5,\ H_2O=28{\cdot}25 \text{ per cent.}$$

It should be understood that the equimolecular is one of the fastest burning of all methane-oxygen mixtures; thus, for example, its rate of detonation—2528 metres per sec.—exceeds that of all other such mixtures, the so-called ‘theoretical’ mixture CH_4+2O_2 having a rate of 2320 only.

SERIES I

Explosion of the Mixture in a Horizontal Glass Tube closed at each end

In this series of experiments a horizontal glass tube 35 cms. long × 2 cms. internal diameter, closed at each end, and provided with platinum-balled electrodes half-way along it (Fig. 51) was first of all thoroughly cleaned, then evacuated by means of a powerful pump, and finally filled at 20° C. and 780 mm. with the moist equimolecular methane-oxygen mixture.* The tap in the capillary end of the tube was then shut. The contents of a number of such tubes were successively ignited by means of a spark of known intensity passed between the electrodes. The intensity of the spark was varied in different trials so as to discover how the subsequent explosions would be affected thereby.

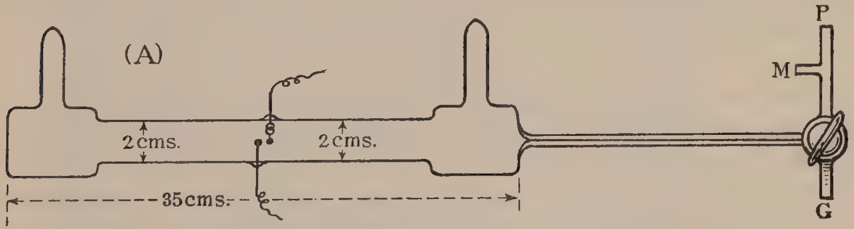

Fig. 51.—Explosion Tube (Series I). (Bone, Fraser and Witt.)
G leads to gas-holder, M to manometer, P to pump.

The course of the resulting explosion in each experiment was photographed upon a highly sensitised film, fastened on a drum which was rotated about its horizontal axis at a constant speed by means of the mechanism already described in Chapter XII., the actual linear speed of the film past the slit behind the lens of the camera being 1540 cms. per sec.

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* The mixture would actually contain about 10 mm. of aqueous vapour.

On ignition, therefore, the flame would start in the neighbourhood of the electrodes, and from thence would be propagated horizontally towards each of the closed ends of the tube. The conditions of ignition were, therefore, approximate to those of open-tube-spark ignition. The photographic record produced on the film would be compounded of the horizontal velocity of the image of the flame in each direction and the vertical movement of the film. The general arrangement and working of the apparatus were the same as that already described in Chapter XII. (Fig. 31 *q.v.*).

In Plate XI. are reproduced four typical photographs so obtained, the only varying conditions being the character and intensity of the igniting spark. The photographs are numbered in order from left to right in accordance with the increasing spark intensity.

Fig. 52 is from an experiment in which a magneto spark across a 1 mm. gap was used for igniting the explosive mixture. The passage of the spark is shewn as a bright spot at the apex of the photograph. A close examination shews that for about 0·00125 sec. after the actual passage of the spark the luminosity (if any) of the gases was insufficient to affect the film, no flame or flame-movement being visible. After this short interval, which is suggestive of an ‘ induction period,’ a feebly actinic ghost-like flame started, and was propagated for a distance of 10 cms. on either side of the igniting spark with a continuous acceleration, but with no appreciable increase in luminosity. The time actually taken for the flame to traverse the first 10 cms. after the commencement of visible luminosity was 0·004 sec., after which a marked deceleration of the velocity always occurred, giving rise to an approximately ‘ uniform flame movement,’ which continued until the flame front reached the closed end of the tube, but without any alteration in the luminosity. At the moment, however, when this ghost-like flame-front reached the end of the tube, a sudden outburst of intense luminosity occurred, as though the greater part of the actual combustion had yet to take place. The whole tube instantly became filled with an intensely luminous flame, traversed by compression-waves, a condition which lasted for at least 0·0025 sec. after the outburst.

We thus have visual evidence of three distinct phases in the explosion, namely (*a*) an initial ‘ induction period ’ of non-luminosity and no flame movement, lasting for about 0·00125 sec. ; (*b*) an intermediate stage of feeble luminosity, extending altogether over about 0·00425 sec., during which each of the two initial flame fronts traversed the medium and reached the closed end of the tube ; and (*c*) a final period of intense luminosity extending over 0·0025 sec. during which, presumably, the main combustion occurred.

PLATE XI.

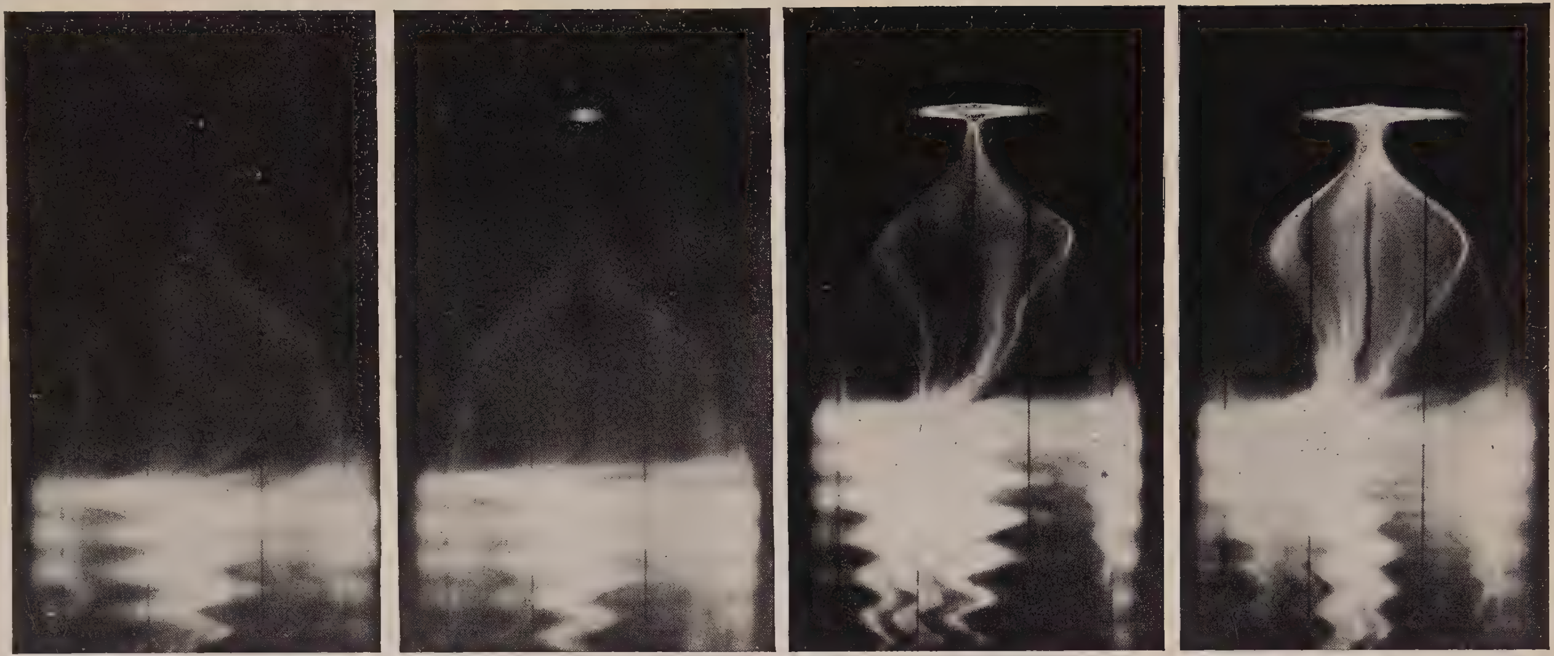
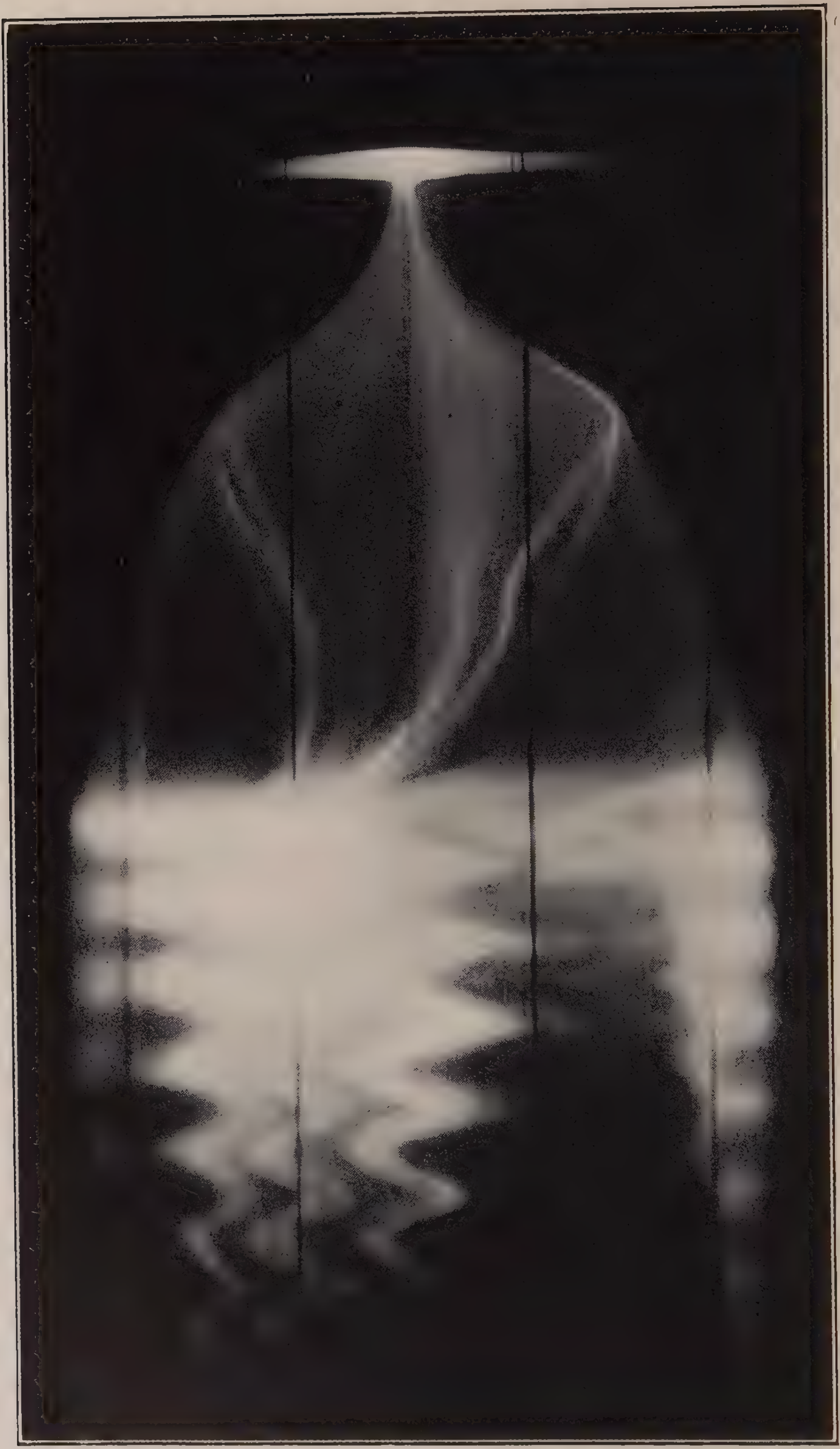


Fig. 52. Fig. 53. Fig. 54. Fig. 55.

Flame Movements in a CH_4+O_2 Mixture ignited at the centre of a closed Tube. (Series I.)

PLATE XII.



Enlarged Record of Flame Movements in a $CH_4 + O_2$ Mixture.

It should be mentioned that a close inspection of the original negative shews features of (*b*) rather suggesting a ‘ composite ’ flame front with three closely-following feebly-luminous flame-bands ; but these are so difficult of reproduction that they are scarcely visible in the print. Also, behind the flame front there are ‘ streamers ’ of gas distinctly more luminous than the surrounding medium, which is almost non-luminous.

Fig. 53 is from an experiment in which almost the minimum condenser-spark-discharge (0·05 microfarad at 1000 volts) was used for ignition. The phenomena associated with the resulting explosion were, in general, much the same as in Fig. 52. The duration of the initial ‘ induction period ’ (*a*) was again about 0·00125 sec., of the first flame phase (*b*) about 0·00425, and of the final period (*c*) of intense luminosity 0·0025 second. In fact, the two photo-records were superposable, the only observable difference between them being that in Fig. 53 the ‘ composite ’ character of the flame-front in (*b*) and the ‘ streamer ’ effects after it were both much fainter.

Fig. 54 is from an experiment in which the igniting source was a condenser-spark-discharge of 3·75 microfarads at 1000 volts. Here quite new features are seen. In the first place, the non-luminous short ‘ induction period ’ (*a*) previously observed is missing, visible combustion starting immediately on the passage of the spark. Next, although the general luminosity of the first flame front (*b*) was still much fainter than that of the final combustion (*c*), it was no longer so homogeneous, being marked by *striæ* of enhanced luminosity whose forward projection was reversed when the initial continuous acceleration of the first-flame front was checked. These ultimately coalesced with the final main combustion (*c*) which had much the same features as the corresponding phases in Figs. 52 and 53. Also, *quite distinct from such striæ*, perfectly straight luminous tracts were discernible in the original negative, suggestive of metallic particles being shot off from the electrodes. The enlargement of this photograph shewn in Plate XII. strengthens this supposition ; on the other hand, the luminous *striæ* referred to suggest streams of ionised gases. Notwithstanding such well-marked differences the average velocity of the first flame front during the phase (*b*), as well as the duration of the phase (*c*), were much the same as in Figs. 52 and 53.

Fig. 55 is from an experiment in which the igniting source was a condenser-spark-discharge of 8 microfarads at 1000 volts. Here the resulting phenomena generally resembled those of Fig. 54, but the *striæ* during the phase (*b*) were much more marked.

It should be pointed out that the marked difference between the appearance of the discharge-spark in Figs. 54 and 55 on the one hand, and Figs. 52 and 53 on the other, is probably due to the much greater ultra-violet emission of the spark in the two first-named cases ; the illumination of the walls of the tube by such an intense emission gave the spark its elongated appearance in the photographs.

There are three outstanding features common to all four experiments, namely (i) that the *average* speed of the ghost-like flame front during the phase (*b*) was much the same in all, (ii) in no case did the main combustion (*c*) commence until the flame front in phase (*b*) had reached the closed end of the tube, and (iii) that its duration was much the same in all cases.

It should be stated that analysis of the products obtained in the various experiments shewed that combustion had been complete in each case.

SERIES II

Explosion of the Mixture in a Horizontal Glass Tube open at each end

In this series of experiments the same mixture was ignited in a horizontal glass tube 50 cm. long × 2·5 cms. diameter (Fig. 56) by a spark passed between lead-electrodes fixed midway along it. The tube had flanged ends, and after it had been evacuated by the pump and filled with the explosive mixture, they were drawn off by a gentle sliding motion immediately before the igniting spark was passed, so thus the resulting explosion took place in an open tube. The linear speed of the film past the slit of the camera was again constant at 1480 cms. per second throughout the series. Plate XIII. (Figs. 57 to 60), shews the results of four typical experiments in each of which the igniting spark was the same as in the corresponding experiment of Series I. Indeed, the only differences between the conditions of the corresponding experiments in Series I. and II. were (i) that in II. the tube was longer and rather wider than in I., and (ii) that in II. both ends of it were *open* instead of being closed as in I.

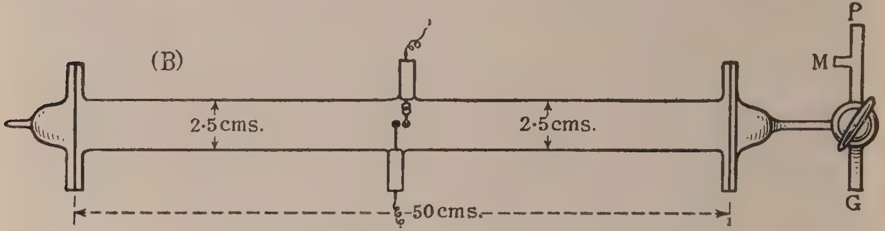


Fig. 56.—Explosion Tube (Series II). (Bone, Fraser and Witt.)
G leads to gas-holder, M to manometer, and P to Pump.

Fig. 57 is from an experiment in which ignition was effected by means of a magneto spark across a 1 mm. gap. Here there was a definite initial non-luminous 'induction period' the duration of which was 0·0012 sec., much the same as in the corresponding experiment (Fig. 52) in the previous series. This was succeeded by the phase (*b*) during which a ghost-like flame front was propagated through the medium with a continuous acceleration almost to the end of the tube. No *striæ* were observable in the photographs, and the intensely luminous phase (*c*), always observed in Series I., was now absent.

Fig. 58 is from an experiment in which the same condenser discharge

PLATE XIII.

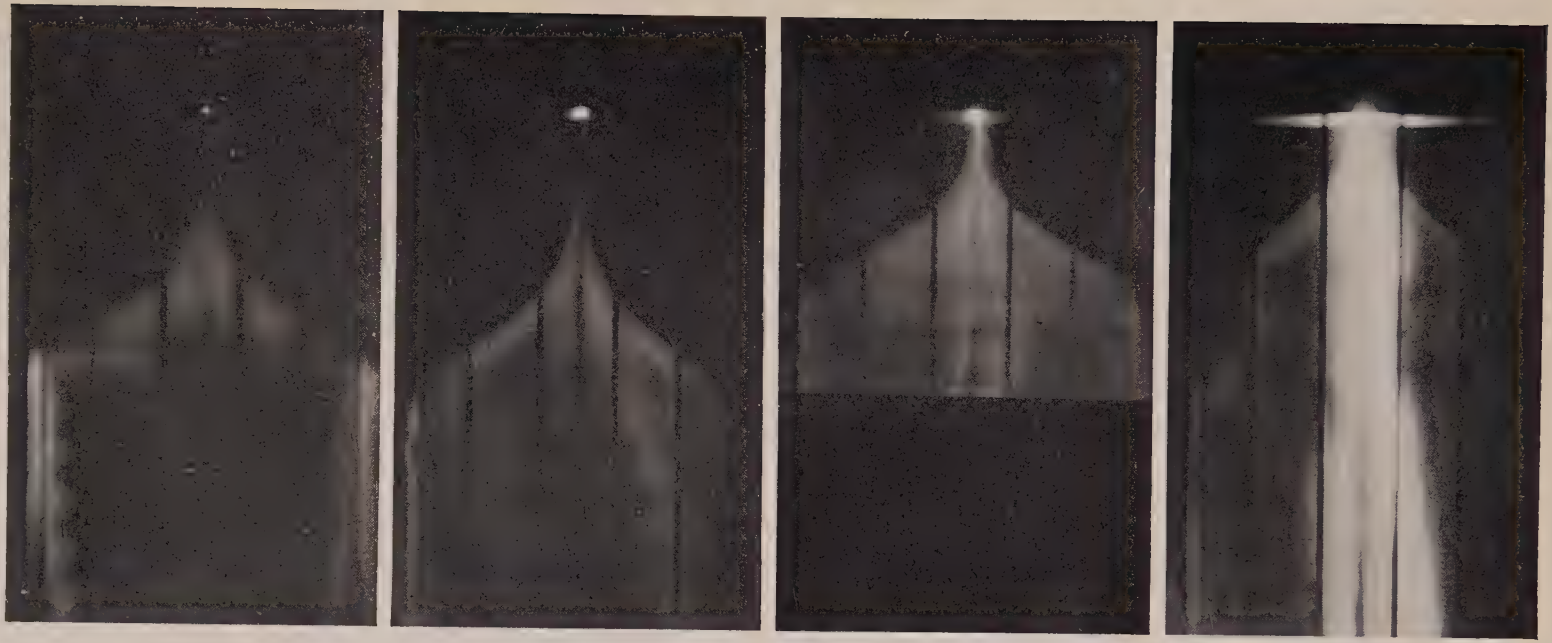


Fig. 57. Fig. 58. Fig. 59. Fig. 60.

Flame Movements in a CH_4+O_2 Mixture ignited at the centre of an open Tube. (Series II.)

PLATE LXIV.

Fig. 62.

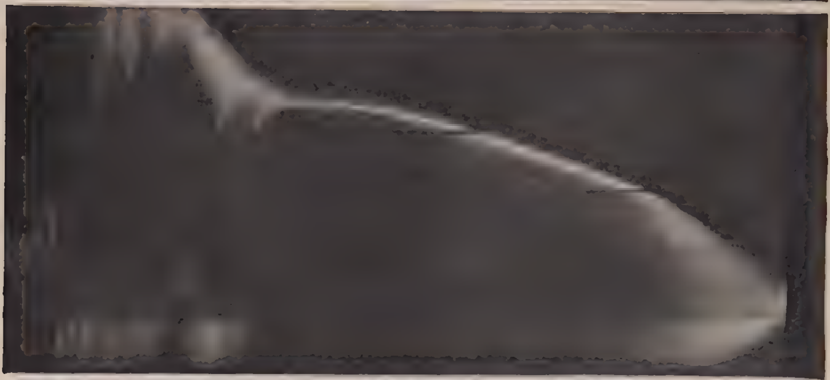


Fig. 63.

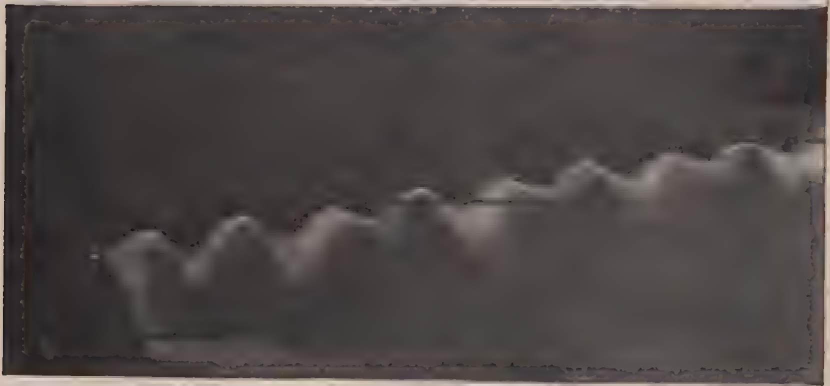


Fig. 64.

Fig. 65.

Flame Movements in a CH_4+O_2 Mixture ignited at the open end of a Glass Tube, the other end being closed.

spark as in Fig. 53 (namely 0·05 microfarad at 1000 volts) was used for ignition. The duration of the non-luminous 'induction period,' before any flame started, was precisely the same as in Series I., Fig. 53. And in most other respects, except the absence of the intensely luminous final phase (*c*), the results were generally the same as in that experiment.

Fig. 59 is from an experiment in which the same condenser discharge-spark as in Fig. 54 (namely 3·75 microfarads at 1000 volts) was used for ignition. Here, as also in Fig. 54, no 'induction period' was observable. The initial flame-movement during phase (*b*) was also much the same in both cases—but now, with the open-ended tube, no phase (*c*) supervened.

Fig. 60 is from an experiment in which the same condenser discharge-spark as in Fig. 55 (namely, 8 microfarads at 1000 volts) was used for ignition. Here an entirely new feature was observed, namely, that combustion immediately started with an intense luminosity in the neighbourhood (*i.e.* in a region of about 5 cm. on either side) of the initiating spark, where it persisted (almost stationary) throughout the whole duration of the experiment. But, beyond such region, only the feebly-luminous ghost-like flame-movement characteristic of phase (*b*) occurred. This is a most significant result, suggestive of the intense combustion characteristic of phase (*c*) being producible by strong 'ionisation' of the reacting gases in the neighbourhood of a powerful initiating spark.

SERIES III

In Plate XIV. is reproduced a series of four photographs obtained in experiments in which the same equimolecular methane-oxygen mixture was ignited at or near the open end of a horizontal glass tube 50 cms. long × 2·5 cms. diameter (Fig. 61), the other end being closed.

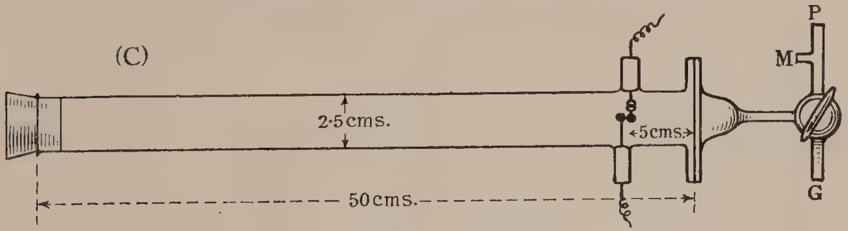


FIG. 61.—EXPLOSION TUBE (SERIES III). (Bone, Fraser and Witt.)
G leads to gas-holder, M to manometer, P to pump.

Fig. 62. Ignition was by means of a 2 cm. high coal-gas flame applied at the open end of the tube. Here we see a long initial 'uniform flame movement' (velocity = 190 cms. per sec.) followed by a well-marked oscillatory movement. The linear film speed past the slit of the camera was 550 cms. per sec.

Fig. 63. Ignition was by means of a powerful condenser-spark-discharge (8 microfarads at 1000 volts) passed between brass point-electrodes at

the mouth of the tube. Here there was (i) a short initial nearly uniform flame movement (velocity = 500 cms. per sec.) succeeded by (ii) an 'oscillatory' movement, during which the mean forward velocity of the flame was decidedly less than in (i) although greater than that observed for the similar phase in the previous experiment with ordinary flame ignition. It should be noted that the speed of the initial uniform movement in this experiment was 500, as compared with only 190 cms. per sec. in Fig. 62, shewing that more than one speed of initial uniform movement can be obtained for the same mixture in the same tube, according to the intensity of the igniting source. The linear vertical speed of the film in this experiment was 220 cms. per second.

Figs. 64 and 65. Ignition was by means of either a magneto (Fig. 64) *or* a powerful condenser spark discharge of 8 microfarads at 1000 volts (Fig. 65) passed between lead balled electrodes fixed inside the tube at a distance of 5 cms. from its open end. In neither case was there any initial uniform movement, the 'oscillatory' movement being set up almost from the first. The intensity of the combustion in the region of the powerful condenser spark used in Fig. 65 is again very marked. The linear speed of the film in each of these experiments was the same as in Fig. 62, namely, 550 cms. per sec.

Concluding Remarks

We think that a careful study of the photographic evidence included in this chapter will convince readers that, notwithstanding all the scientific investigation of the matter since Mallard and Le Chatelier first took it up in the year 1880, we have still much to learn about the initial stages of gaseous explosions. Indeed a systematic reinvestigation of the whole subject now seems called for, and it is proposed to continue these experiments in the hope of elucidating further the new features which have been disclosed so far.

Therefore, we wish it to be understood that in this chapter we are merely describing, as best we can, the phenomena which have been observed, and which are recorded in the photographs. At present we are content with directing attention to their outstanding features, and indicating their significance, without attempting to explain them. We have used the terms 'induction period' and 'ghost-like flame' as being the best we could find to describe what the photographs show, leaving it to further investigation to discover what interpretation must be given to them. It cannot yet be said what proportion of the total combustion occurs during the passage through the explosive medium of the 'ghost-like' flame observed in Series I. and II.; presumably, however, from the appearance of the photographs, it is relatively small. This, and many other points, must await further experimental investigation which is now being undertaken.

CHAPTER XV

THE DEVELOPMENT OF DETONATION IN GASEOUS EXPLOSIONS

Berthelot and Vieille's Discovery of 'l'Onde Explosive'

It was in the year 1881 that Berthelot and Vieille,* and independently also Mallard and Le Chatelier,† announced in the *Comptes Rendus* their discovery of the rapid acceleration of the initial flame speed in gaseous explosions and the final attainment of the enormously higher constant velocity of the explosion wave ('*l'onde explosive*'). Since that time the phenomena associated with the development of 'detonation' and the propagation of 'the explosion wave,' have been extensively studied in this country by H. B. Dixon and his co-workers,‡ whose researches will be reviewed in this and the next chapters.

Berthelot and Vieille made the very important discoveries (i) that when a gaseous explosive mixture is ignited in a closed tube at atmospheric temperature and pressure the resulting flame speed is usually rapidly accelerated from its point of origin until it reaches a maximum which remains constant however long the column of gases may be, and (ii) that each particular explosive mixture has its own definite maximum 'rate' of explosion. They termed the flame when propagated at such maximum velocity through an explosive mixture, '*l'onde explosive*,' and described it as "*une certaine surface régulaire où se développe la transformation, et qui réalise un même état de combinaison, de température, de pressure, etc. Cette surface, une fois produite se propage ensuite, de couche en couche, dans la masse tout entière, par suite de la transmission des chocs successifs des molécules gazeuses amenées à un état vibratoire plus intense en raison de la chaleur degagée dans leur combinaison, et transformée sur place, ou plus exactement, avec un faible déplacement relatif. . . .*"

Such conditions are comparable with those of a sound wave passing through the gaseous medium, with, however, the important difference that whereas a sound wave is propagated from layer to layer with a small compression, and a velocity determined solely by the physical condition of the vibrating medium, in the explosion wave an abrupt change in chemical conditions is propagated which generates an enormous force as it passes through each successive layer of the medium.

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* Also *Ann. Chem. Phys.* (5), xxviii. pp. 289 to 332.

† Also *Ann. des Mines* (8), iv. pp. 335 to 338.

‡ *Phil. Trans.* **184** (1893), pp. 97–188, and A. **200** (1903), pp. 315–352.

In their experimental work Berthelot and Vieille proved that the velocity of the 'explosion wave' is quite independent of the length of the column of gas traversed, and of the material and diameter of the tube employed, provided a certain small limiting diameter is exceeded; also, that it is immaterial whether the tube is laid out straight, coiled round a drum, or even zigzagged. They also concluded that the velocity is independent of the pressure, but this is not strictly correct; for, as H. B. Dixon subsequently shewed, the rate increases slightly with pressure up to about two atmospheres, when it becomes nearly constant. They term it "*une propriété fondamentale ; car elle établit que la vitesse de propagation de l'onde explosive est régie par les mêmes lois générales que la vitesse du son.*"

In determining such 'rates of explosion' Berthelot and Vieille fired the explosive mixture in a closed leaden tube, so arranged that, after a run sufficiently long to ensure the setting up of the explosion wave, the flame broke two bridges of tin foil, at a convenient distance apart, each of which formed part of an electric circuit connected with a suitable chronographic recording arrangement.

In illustration of their experiments proving the constancy of the rate of explosion for an explosive mixture, the following results for electrolytic gas ($2H_2 + O_2$) at atmospheric temperature and pressure may be cited.

TABLE XLI.—BERTHELOT AND VIEILLE'S DETERMINATION OF THE RATE OF EXPLOSION OF ELECTROLYTIC GAS

Experimental Arrangement.	A. Horizontal Straight Lead Tube 42·45 Metres long, 5 mm. Internal Diameter.		B. Horizontal Straight Lead Tube 30·4 Metres Long, 15 mm. Internal Diameter.	C. Same Tube as in A, but zigzagged.	D. Caoutchouc Tube 40·1 Metres Long, 5 mm. Internal Diameter.
Rate of explosion in metres per sec.	2901	2675	2754	2860	2685
	2908	2877	2975	2712	2911
	3051	2872	3019	2791	2994
	2821	2783			2672
					2788

With the caoutchouc tube referred to, it was shewn that, so long as it was filled with electrolytic gas under the same conditions, it did not matter much whether, at the moment of firing, the ends were closed or open, as the following figures indicate :

	Rate of Explosion for $2H_2+O_2$ in Caoutchouc Tube. Metres per sec.
(1) End nearest firing plug open	2645
(2) End farthest from firing plug open	3052
(3) Both ends open	2766
(4) Both ends closed	2821

Berthelot and Vieille distinguished between two limiting conditions of gaseous combustion, namely : (1) *ordinary flame propagation*, in which the heat developed by the chemical change is mainly lost by radiation, conduction, and by contact with inert gas, except the small part required to raise the next layer to its ignition temperature, and (2) *detonation*, in which the heat of chemical change is transmitted adiabatically to the next layer. Between such limits a whole series of intermediate states may conceivably intervene, "*mais elles ne constituent aucun régime regulier—En effet, le passage d'un régime à l'autre est accompagnie, comme il arrive en général dans les transitions de cette espèce, par des mouvements violents des déplacements de matière étendus et irreguliers, pendant les quels la propagation de la combustion s'opère avec une vitesse de plus en plus considerable.*"

In general, they thought that, for a given series of explosive mixtures, the range of 'inflammability' is wider than that of 'detonation'; thus, whereas for hydrogen-air mixtures the lower limit of inflammability at atmospheric temperature and pressure is reached when the mixture contains only 4·1 per cent. of hydrogen, they found that the lower limit of detonation was not reached until it contained as much as 23 per cent. of hydrogen. This supposition has recently been confirmed by W. Payman * for methane-oxygen mixtures; he found that whereas the 'range of inflammability' at atmospheric temperature and pressure for such mixtures is between the limits of 5·7 and 59·2 per cent. of methane, the 'range of detonation' is much narrower, namely, between 11·1 and 53·3 per cent. of methane respectively.

Berthelot and Vieille assumed that the velocity of the explosion wave equals, or approximates closely to, the mean velocity of translation of the molecules at the moment of combination, supposing them to retain all the heat developed in the reaction, as calculated from the Clausius formula :

$$v=29{\cdot}354\sqrt{\frac{T}{d}},$$

where $T=$ the maximum temperature (abs.) reached in the explosion ; and $d=$ the density of the products of combustion referred to air.

They assumed $$T=\frac{Q}{n\times 6{\cdot}8},$$

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* *Trans. Chem. Soc.* 115 (1919), p. 1436.

where Q = the heat produced by the chemical change, and

n = the number of 'molecular-volumes' of gases taking part in the reaction.

Thus, in calculating T, it was assumed (i) that the gases are heated at *constant pressure* (which surely is not the case), and (ii) that the specific heat of a compound gas is the sum of the specific heats of its constituents (which, again, is wrong).

How the values so calculated by Berthelot and Vieille compared with those actually found by them is shewn in the following table :

TABLE XLII.—BERTHELOT AND VIEILLE'S RESULTS FOR RATES OF EXPLOSION

Mixture Fired.	d.	Q calc.	T.	v in Metres per sec.	
				Calculated.	Found.
$2H_2+O_2$	0·622	59,000	5,780°	2831	2810
$2CO+O_2$	1·529	68,200	6,700°	1941	1089
$2C_2H_2+5O_2$	1·227	308,000	10,070°	2660	2482
$2C_2H_6+7O_2$	0·985	359,300	7,050°	2483	2363
$C_2H_4+3O_2$	1·075	321,400	7,880°	2517	2209
CH_4+2O_2	0·924	193,500	6,320°	2427	2287
$C_2N_2+2O_2$	1·343	262,500	9,650°	2490	2195

It should be noted that some of the rates found did not agree very well with those calculated from the formula; indeed Berthelot and Vieille considered it to be 'provisional' only, for in commenting upon the above results they remarked : "*En somme, la vitesse de translation des molécules gazeuses, conservant la totalité de la force qui répond à la chaleur dégagée par la réaction peut être regardée comme une limite representant la vitesse maxima de propagation de l'onde explosive. . . . Mais cette vitesse est diminuée par la contact des gaz et autres corps étranges ; elle l'est également lorsque la masse enflammée au début est trop petite et trop rapidement refroidée par rayonnement ; elle l'est encore lorsque la vitesse élémentaire de la réaction chimique est trop faible, comme il paraît arriver avec oxyde de carbone. Dans ces conditions, il y a ralentissement de l'onde, et celle-ci peut même cesse de se produire ; la combustion se propageant alors de proche en proche suivant une loi beaucoup plus lente.*"

It is also important to observe that they were of the opinion that dissociation plays hardly any part in the phenomena of the wave, owing to the high pressures developed in it, and its extremely short duration.

The principal conclusions reached by Berthelot and Vieille may be summarised in two sentences, namely: (i) that the velocity of the explosion wave is a true physical constant for each particular inflammable mixture, and (ii) that the wave is propagated by the impact of the products of combustion of one layer upon the unburnt gases in the next at the mean velocity of translation of the burnt gaseous molecules, retaining the whole heat developed in the reaction, which, however, is to be regarded as a *limit* representing the *maximum* possible rate of propagation, and therefore subject to diminution in particular cases.

H. B. Dixon's Photographic Researches

H. B. Dixon began his researches into the explosion wave very soon after the publication of Berthelot and Vieille's classical memoir in 1883, and has continued them ever since. His work falls into two categories, namely : (i) the measurement of rates of explosion, which chiefly occupied him during the first ten years, and (ii) photographic investigations, which were carried out mostly between 1895 and 1903. For the greater part they were published in the *Philosophical Transactions of the Royal Society* in the years 1892 and 1903. For the purpose of this review, however, it will be best to consider first of all the later photographic experiments, because they give visual evidence both of how detonation is set up and of some characteristics of the ' explosion wave.' We shall then be in a better position to deal with the earlier determinations of ' rates ' of explosion.

His photographic researches were carried out at Owens College, Manchester University, principally in conjunction with E. H. Strange and E. Graham,* from the year 1895 onwards, the first description of their method being given in a paper, entitled " On the Explosion of Cyanogen," which was read at the Chemical Society in the year 1896. A complete memoir was subsequently published in the Royal Society in 1903 (*loc. cit.*). Meanwhile Berthelot and Le Chatelier had been working together on similar lines in France, and published papers in 1899 and 1900.†

The method employed (shewn diagrammatically in Fig. 66) was essentially that of Mallard and Le Chatelier, with such improvements as the rapid advance of photographic art had made possible. A highly sensitive ' Eastman ' film was fixed on the periphery of a light metal drum or wheel, 1 metre in circumference, rotated in a vertical plane by means of an electric motor at a constant maximum speed of 6000 revolutions per minute, which meant that the film itself would move at a maximum constant speed of 100 metres per second, although usually only about half this speed was employed. The explosion tube was placed horizontally at such a distance from the camera that the length of the image was one-thirtieth that of the tube. Hence, a flame actually travelling horizontally in the tube with a velocity of (say) 3000 metres per second would give an image travelling along the film at the rate of 100 metres per second. The true linear velocity of the film was determined in each experiment by means of a tuning fork. Subsequently the films were slowly developed, in one to three hours, in a long trough kept rocking by suitable gear; after being fixed and washed they were finally soaked in glycerine and water to prevent them curling up on drying.

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* H. B. Dixon, E. H. Strange and E. Graham, *Trans. Chem. Soc.* **69** (1896), pp. 759 to 774.

† Berthelot and Le Chatelier, *Comptes Rendus*, **129** (1899), p. 427 ; also Le Chatelier, *ibid.* **130** (1900), p. 1755.

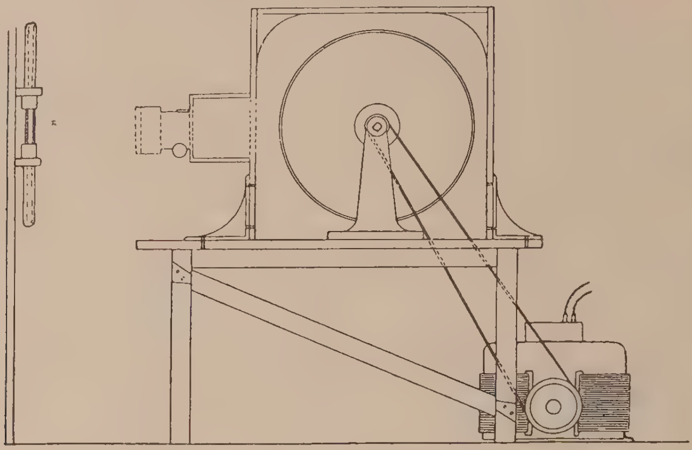

Fig. 66.—H. B. Dixon's Apparatus.

In this way it was possible to analyse photographically the phenomena concerned in the development and propagation of detonation in gaseous explosions, as well as the secondary effects produced when explosion waves meet in collision. From the graph traced photographically by the flame on the film its velocity at any instant could be calculated by means of a simple formula, as follows:

If AB = the horizontal velocity of the flame-image v_1,
AC = the vertical velocity of the film v_2
and α = the angle which the resultant graph makes with the horizontal.

Then $$v_1 = \frac{v_2}{\tan \alpha}.$$

And the actual flame velocity $= \dfrac{30v^2}{\tan \alpha}$.*

It is impossible in the space at our disposal to give any adequate idea of the wealth of information contained in the very beautiful series of over seventy photographs of explosion flames included in Dixon's memoir (*loc. cit.*). All that we can do is to reproduce a few examples in the hope of so stimulating the reader's interest in the subject that he will study thoroughly the original memoir, which is the only way to a real understanding of its value.

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* Because the apparatus was so arranged that the actual length of the explosive tube =30 times that of its image when focussed on the film.

The development of an explosion in the gaseous mixtures $CS_2 + 5O_2$, fired by a spark a few inches from the closed end of a tube, is very clearly shewn in the photograph reproduced in Fig. 67—which is analysed in Fig. 68. The igniting spark in starting the explosion at *O* sends out invisible compression waves in both directions along the tube; these traverse the unburnt gases in advance of the flame with the velocity of sound, as indicated by the dotted lines *OM*, *ON* in the diagram. The flame itself, travelling at first more slowly than the compression waves, traces the curves *OA* and *OB*. The compression wave *ON*, on reaching the closed end of the tube, is reflected back again as *NC*, and, on meeting the flame (which is still travelling in the direction *OA*), retards it, and passes thence through the hot and still burning gases as the visible wave *CD*. An instant later it overtakes, at *D*, the front of the flame travelling in the direction *OB*, thereby accelerating it, and increasing its luminosity in consequence of the quickened combustion. The flame then continues to move forward from *D* with rapidly accelerated velocity until 'detonation' is finally set up at the point *E*, near where the flame catches up with the compression wave *OM*. Indeed, it is the forward 'kick' received

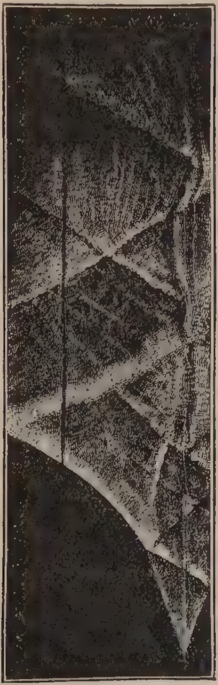

FIG. 67.—DEVELOPMENT OF AN EXPLOSION IN A $CS_2 + 5O_2$ MIXTURE.

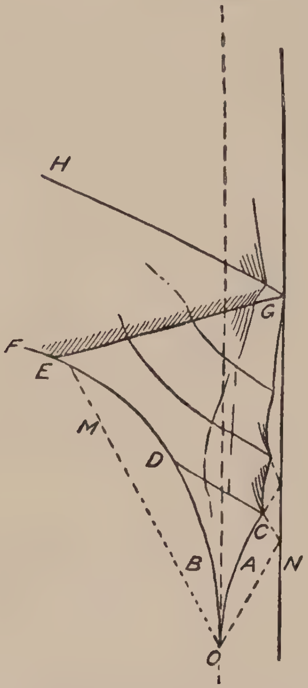

FIG. 68.—ANALYSIS OF SAME.

by the already accelerated flame front on its overtaking the compression wave *OM* which finally determines 'detonation.' At the instant when 'detonation' is set up the flame attains its final constant velocity, and the combustion and luminosity their maximum intensities; simultaneously, a strongly luminous wave of compression *EG* (called the 'retonation wave') is sent backwards through the still burning gases, which on reaching the near end of the tube is reflected back as *HG*. The 'detonation' wave *EF* passes onwards through the mixture with its characteristic high velocity and intense luminosity.

It should be noted that the discovery that a backward 'retonation wave' is always set up when 'detonation' is determined in a gaseous explosive mixture was made independently in the year 1900* by Le Chatelier, who said, "*Au moment du développement spontané de l'onde explosive une onde condensée rétrograde est toujours lancée en arrière dans les gaz déjà brûlés*"; some of Dixon's photographs shewing the 'retonation wave' had already been published in Manchester in the year 1898. Both Le Chatelier and Dixon had independently discovered the setting up of a 'reflexion wave' ('*une onde condensée réfléchie*') when a detonation wave is arrested by the *closed* end of a tube, or by a constriction in it.

Le Chatelier had also observed that "*au point de rencontre d'ondes explosives allumées simultanément en différentes parties d'une masse gazeuse, leur extinction simultanée donne naissance à des ondes condensées prolongées qui progressent dans la même direction que les ondes explosives aux quelles elles succèdent.*"

Thus, in studying gaseous explosions, it is necessary to distinguish between (i) the 'detonation wave' ('*l'onde explosive*'), (ii) the 'retonation wave' ('*l'onde rétrograde*'), (iii) the 'reflexion wave' ('*l'onde réfléchie*'), and (iv) the 'collision wave' ('*l'onde prolongée*'), whose velocities through the medium are in the order given, that of 'detonation' being the highest, as the following determinations by Le Chatelier for an equimolecular mixture of acetylene and oxygen ($C_2H_2 + O_2$) indicate:

	Metres per second.
Detonation-wave	2990
Retonation-wave	2300
Reflexion-wave	2250
Collision-wave	2050

Except in special circumstances (*e.g.* when it is reinforced by another reflected wave) the velocity of the 'retonation wave' is always inferior to that of the 'detonation wave.' When, however, the 'retonation wave' is developed just at the closed end of a tube it may be reinforced by a 'reflexion wave,' in which case its velocity is indistinguishable from that of true detonation.

In many of his experiments Dixon employed cyanogen-oxygen mixtures

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* *Comptes Rendus*, **130** (1900), p. 1755.

PLATE XV.

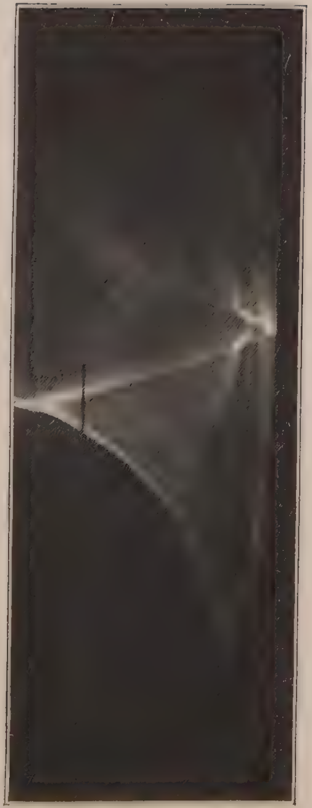

FIG. 69. DEVELOPMENT OF AN EXPLOSION IN A $C_2N_2 + 2O_2$ MIXTURE.

FIG. 70.—DETONATION WAVE PASSING THROUGH AN EXPLOSIVE MIXTURE.

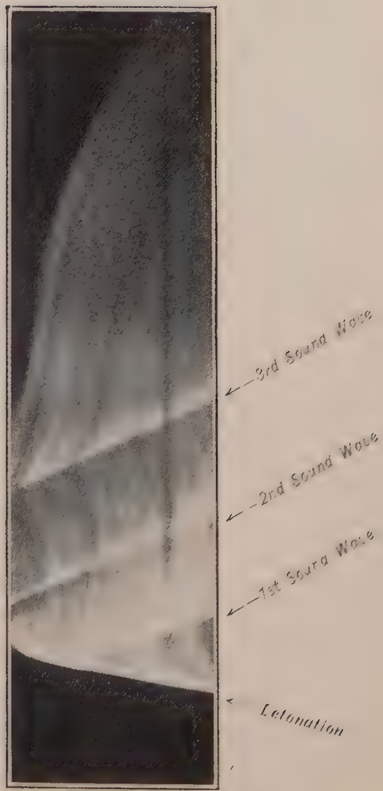

FIG. 71. SOUND WAVES MEETING DETONATION OF A $C_2N_2 + 2O_2$ MIXTURE.

PLATE XVI.

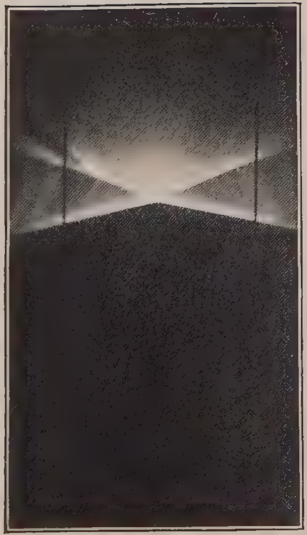

Fig. 72.—Collision of two Detonation Waves in a $C_2N_2+2O_2$ Mixture.

Fig. 73.—Retonation Wave started at end of tube.

Fig. 74.—Retonation Waves formed by Explosion in centre of long tube.

Fig. 75.—Two Explosions Meeting.

PLATE XVII.

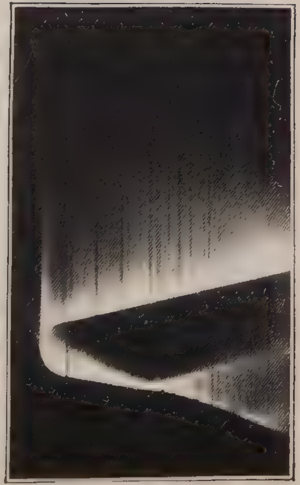

Fig. 76.—Detonation Wave passing round a glass bend.

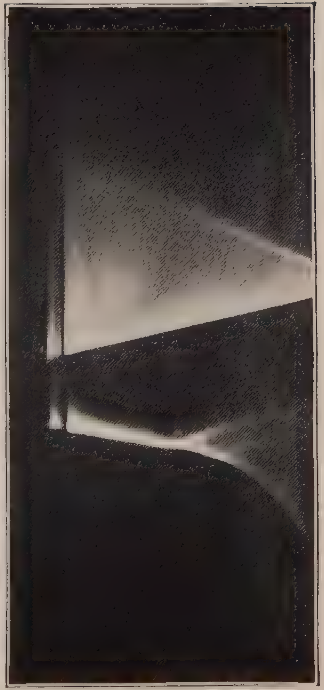

Fig. 77.—Detonation Wave passing through flexible rubber Junction without retardation.

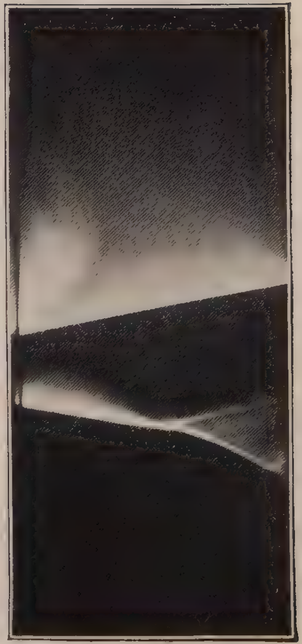

Fig. 78.—Detonation Wave passing through rigid copper Junction without retardation.

whose compositions were either $C_2N_2+O_2$ or $C_2N_2+2O_2$; and, in considering them, it is necessary to remember that in the detonation wave itself the cyanogen is burnt to carbonic oxide only, in accordance with the equation:

$$(a)\ C_2N_2+O_2=2CO+N_2,$$

the completion of the combustion to carbonic acid taking place comparatively slowly in the region immediately *behind* the wave, in accordance with the equation

$$(b)\ 2CO+N_2+O_2=2CO_2+N_2.$$

The following selection from Dixon's published photographs (see Plates XV., XVI. and XVII.) illustrates some of the foregoing features:

Fig. 69 shews the initial stages, up to detonation, in the explosion of a $C_2N_2+2O_2$ mixture fired by a spark near the closed end of a horizontal tube. It should be noted (i) how the reflected sound waves from the closed end of the tube check the progress of the flame towards that end; (ii) how, as the velocity of the flame towards the other end is continuously accelerated, its luminosity increases; and (iii) how, at the moment when detonation is set up, a retonation wave is thrown back through the still burning gases behind the flame front, intensifying their combustion, and making a luminous track through them; the wave is reflected on reaching the closed end of the tube, and continues for some distance in a luminous track through the still burning mixture.

Fig. 70 shews a detonation wave passing through an explosive mixture; its uniform velocity should be noted, as also the swirling of the gases immediately behind it.

Fig. 71 shews a series of sound waves, originating at the *far* end of the tube, meeting the detonation wave in a $C_2N_2+2O_2$ mixture travelling towards that end.

Fig. 72 shews the end-on collision of two detonation waves in a $C_2N_2+2O_2$ mixture.

Fig. 73 shews a retonation wave started at the end of a tube.

Fig. 74 shews retonation-waves resulting from an explosion which was started in the centre of a long tube.

Fig. 75 shews the end-on collision of two explosion flames traversing, in opposite directions, a mixture in which detonation had not been determined; this should be contrasted with Fig. 44, in which two detonation waves are shewn similarly colliding. It should be noted that when the two explosion flames in which detonation had *not* been developed collided, they gave rise to two reflected waves each more rapid and luminous than the incident ones. This would be explained by supposing that the initial period of an explosion is distinguished from detonation not only by a slower flame propagation but also by a much less intense combustion generally.

Figs. 76 to 78 (inclusive) are explained on the Plate.

The explanation of the intense luminosity of the ‘detonation wave,’ and its higher velocity than that of sound through the exploded gases, is that the combustion during the initial stages of an explosion is always very much slower than after ‘detonation’ has been set up. Under the extreme conditions of ‘detonation’ it is probable that the temperature of each successive layer of the explosive mixture is suddenly raised to the ignition point by adiabatic compression, and that a larger proportion of the collisions between chemically opposite molecules is fruitful of change; intense ionisation of the gases by ‘collision,’ as also radiation, may possibly play a part, but as yet we know far too little about the matter to make any assertions. It is, however, tolerably certain that in detonation the chemical actions concerned in the propagation of the flame front are completed in an immeasurably short time. Many years ago W. A. Bone and B. Lean, working in Dixon's laboratory in Manchester, found by a photographic method that the duration of luminosity in each successive layer of gas in the detonation of electrolytic gas is certainly less than $\frac{1}{5000}$ second, and possibly as short as $\frac{1}{10000}$ second;* this means that the whole duration of the chemical reaction *plus* some cooling of the product was of extremely short duration indeed, much shorter than the time required to shatter the thin glass test-tube attached to the end of the explosion coil used. This tube, though invariably smashed to powder by the force of the explosion, always appeared perfectly intact in the photograph, shewing that the luminosity of the explosion had vanished before its force had time to shatter the thin glass test-tube.

Taking the evidence as a whole, therefore, there can be little doubt but that during the initial stages of an explosion the combustion *in the flame front* is comparatively slow and incomplete, so that its propagation is comparatively slow, and much combination goes on behind it. In detonation, on the other hand, the chemical changes *concerned in the propagation of the wave fronts* are practically instantaneous; albeit, when a gas burns in *stages*, only the first of them may actually be concerned in the wave front, as in the combustion of cyanogen, which definitely proceeds in two stages. There can also be no doubt as to the important rôle played by compression waves in determining ‘detonation’ in gaseous explosions, and as to ‘collision waves,’ etc., being largely responsible for their violent shattering effects.

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* *British Association Reports*, 1892.

CHAPTER XVI

DETONATION (*Continued*)—RATES OF EXPLOSION—THEORY OF THE EXPLOSION WAVE

H. B. Dixon's Researches on Rates of Explosion

The method employed by H. B. Dixon in his classical work on rates of explosion was in principle the same as that designed by Berthelot (*q.v.*). His explosion tube was a leaden tube 100 metres long and 9 mm. internal diameter, except for very violent mixtures, when a stronger tube of the same length but 6·5 mm. internal diameter was substituted. It was closed at each end by a steel stopcock, and fitted at one end with a stout glass 'firing piece' for the ignition of the explosive mixture by an electric spark. It was then coiled round a drum 2 ft. in diameter, and immersed in water contained in a circular trough. The velocity of the explosion wave was measured by timing the flame between two bridges of silver foil, each of which was connected in an electric circuit with an electromagnetic stylus recording on a chronograph. The first bridge was situated about four feet away from the firing wires, in order to allow the flame a sufficient preliminary run from the setting up of detonation before it reached the bridge. The second bridge was placed near the other end of the tube. Fig. 79 gives a plan of the experimental arrangements; for further details the original memoir should be consulted.*

The chief differences between Dixon's procedure and that of Berthelot were (i) his explosion tube was longer and wider, (ii) his 'bridges' were of silver instead of tinfoil, (iii) he used no fulminate for igniting his mixture, and (iv) after ignition the flame was allowed a longer run (about four feet) before it reached the first bridge, a precaution which in some cases was found to be essential.

It should be noted here, that on ignition by means of an electric spark, the distance which the flame must travel through a gaseous explosive medium before detonation can be set up has been found to depend on several factors, such as the composition and pressure of the explosive medium, the diameter of the tube, and the distance of the igniting spark from the closed end; on the other hand, if the mixture be fired by means of a 'high explosive,' such as a small fulminate charge, detonation is set up generally almost immediately, a short period only of non-uniform flame movement intervening. Thus in the case of electrolytic gas, with ordinary spark ignition, in one and the same apparatus, Dixon found a distance of 12 inches was required when the igniting spark was 3 inches from the closed end of the tube; but with a spark quite close up to the end a distance of 4 feet was required. With a mixture of cyanogen and

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* *Phil. Trans.* 184 (1893), pp. 103 to 106, and 169 to 176.

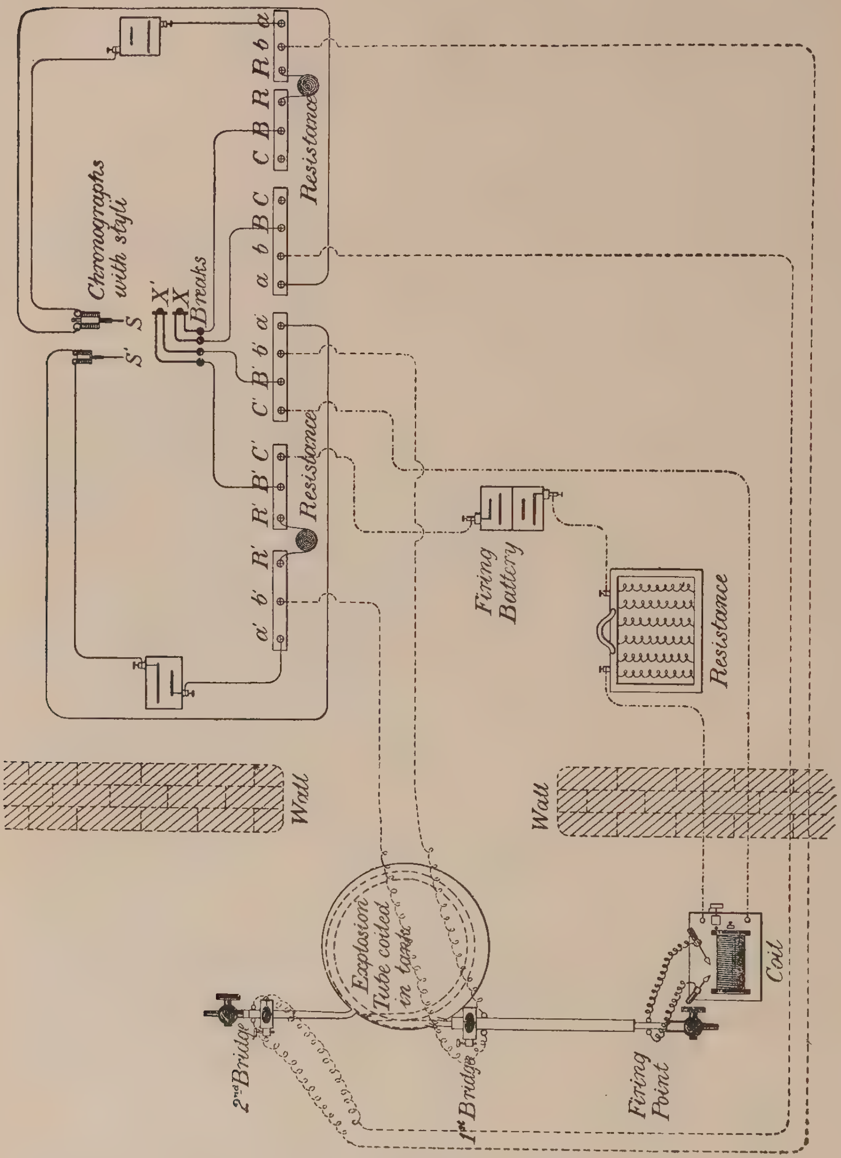

Fig. 79.—H. B. Dixon's Apparatus for determining Rates of Explosion.

oxygen ($C_2N_2+2O_2$) the distances similarly found were 10 and 12 inches respectively.

Dixon first of all confirmed Berthelot's conclusion that the explosion wave has a constant velocity for one and the same explosive mixture, at a given temperature and pressure, which is independent of the material or diameter (beyond a certain limit) of the tube, and of the way it is arranged. Thus in thirty-two different experiments with electrolytic gas ($2H_2+O_2$) at ordinary temperature and pressure, using tubes of 9 mm. and 6·5 mm. diameter, sometimes laid straight out and at other times coiled round a drum, he found rates varying between 2781 and 2852 metres per second only, with a general mean of 2820 metres per second.

He next tested the influence of temperature and pressure, respectively, upon the rates of explosion of various mixtures, finding that, whereas an increase in the initial temperature from 10° to 100° depressed the rate very slightly, it increased with the initial pressure up to a certain crucial pressure, which for electrolytic gas is about two atmospheres, afterwards becoming independent of pressure. The following results will serve to illustrate those points :

(1) *Rates of Explosion for Electrolytic Gas at various Temperatures and Pressures*

(*a*) At 10° C.

Pressure -	200	300	500	760	1100	1500	mm.
Rate - -	2627	2705	2775	2821	2856	2872	metres per sec.

(*b*) At 100° C.

Pressure -	390	500	760	1000	1450	mm.
Rate - -	2697	2738	2790	2828	2842	metres per sec.

(2) *Rates of Explosion for* H_2+N_2O *Mixture at* 10° C.

Pressure -	500	760	1000	mm.
Rate - -	2094	2305	2302	metres per sec.

(3) *Rates of Explosion for* CH_4+2O_2 *Mixture at* 10° C.

Pressure -	500	760	1000	mm.
Rate - -	2280	2322	2319	metres per sec.

(4) *Rates of Explosion for* $C_2H_4+2O_2$ *Mixture at Atmospheric Pressure*

Temperature - - - -	10° C.	100° C.	
Rate - - - - - -	2581	2538	metres per sec.

Dixon's principal objective was to investigate how rates of explosion vary with the chemical compositions of explosive mixtures, and particularly to discover the effects of diluting detonating mixtures with either nitrogen, or excess of one or other of the reacting gases, with a view of elucidating the mechanism of the combustion of various gases. In this connection it is necessary to bear in mind the importance of distinguishing in each case between (*a*) the initial reaction in the wave itself, which alone is concerned in its propagation, and (*b*) reactions which may take place in the rear of the wave, and are not concerned in its propagation, because the combustion of many gases (*e.g.* cyanogen, and hydrocarbons generally) proceeds in definite stages, and usually only the initial stage occurs in the wave itself, the others continuing in the still burning mixtures behind it. We will now consider some typical cases in the light of Dixon's results.

Rates for Hydrogen and Oxygen Mixtures

The effects of diluting electrolytic gas either with nitrogen or with excess of one or other of the reacting gases, were found to be as follows :

Rates at Atmospheric Temperature and Pressure in Metres per second

Electrolytic gas $2H_2+O_2$ 2821	$2H_2+O_2+2H_2$ 3268	$2H_2+O_2+4H_2$ 3527	$2H_2+O_2+6H_2$ 3532
	$2H_2+O_2+O_2$ 2328	$2H_2+O_2+3O_2$ 1927	$2H_2+O_2+5O_2$ 1707
	$2H_2+O_2+N_2$ 2426	$2H_2+O_2+3N_2$ 2055	$2H_2+O_2+5N_2$ 1815

In this case the primary reaction $2H_2+O_2$ is probably nearly completed in the wave itself, dissociation having but little or no influence upon the rate of explosion ; because dilution with excess oxygen retards the wave a little more, by virtue of its greater density, than similar dilutions with nitrogen. Progressive dilution with excess of hydrogen increases considerably the rate of explosions, an effect due principally to the density of the medium being greatly reduced by the addition of hydrogen, as will be explained later.

Rates shewing the Mode of Combustion of Cyanogen

Perhaps the most important conclusion established by Dixon's experiments was that cyanogen burns in two well-defined stages, namely : (i) primarily to carbonic oxide in the wave itself, and (ii) afterwards to carbon dioxide behind it. For it was found not only that the equimolecular mixture $C_2N_2+O_2$ had the highest rate of explosion, but also that its dilution with oxygen had a greater retarding effect than a corresponding

PLATE XVIII.

A. Explosion of a $C_2N_2+O_2$ Mixture taken on a stationary film.
B. Explosion of a $C_2N_2+O_2$ Mixture taken on a moving film.
C. Explosion of a $C_2N_2+O_2+N_2$ Mixture taken on a moving film.
D. Explosion of a $C_2N_2+2O_2$ Mixture taken on a moving film.

dilution with nitrogen, clearly shewing that any oxygen in excess of the equimolecular proportion is inert in the wave itself, thus :

$$\begin{array}{c} C_2N_2+O_2 \\ 2728 \end{array} \left\{ \begin{array}{cc} C_2N_2+2O_2 & C_2N_2+3O_2 \\ 2321 & 2110 \\ C_2N_2+O_2+N_2 & C_2N_2+O_2+2N_2 \\ 2398 & 2166 \end{array} \right\} \text{metres per second.}$$

Therefore, it follows that when detonation occurs in a mixture $C_2N_2+2O_2$, *i.e.* one containing just sufficient oxygen to burn the carbon completely to the dioxide, the combustion proceeds in two stages, namely :

(i) $C_2N_2+2O_2=2CO+O_2+N_2$, in the wave itself,

and (ii) $2CO+O_2+N_2=2CO_2+N_2$, behind the wave.

This conclusion was driven home by Dixon, in conjunction with Strange and Graham, by photographing on a sensitive film, rotated at a speed of about 1500 metres per minute, the explosion flame in the case of the three mixtures (*a*) $C_2N_2+O_2$, (*b*) $C_2N_2+O_2+N_2$ and (*c*) $C_2N_2+2O_2$. In each case the flame was photographed, after detonation had been set up, as it dashed past a glass window inserted into the lead explosion coil.* The image obtained in the case of (*a*) showed an intensely brilliant flame (the explosion wave), slightly drawn out in tapering form ; in the case of (*b*), with nitrogen as diluent, the flame was less brilliant and somewhat more drawn out than in (*a*) ; but with (*c*) the flame, whilst no more luminous than in (*b*), was drawn out to great length, owing to the continued combustion of carbon monoxide in the rear of the wave. The photographic reproduction in Plate XVIII (approximately to scale), will convey an idea of the relative durations of the flames in the three cases.

Rates shewing the Influence of Steam in the Combustion of Carbonic Oxide

As long ago as 1880 Dixon had made the important discovery, the significance of which will be fully discussed in a later chapter, that a mixture of carbonic oxide and oxygen, dried by long contact with phosphoric anhydride, will not explode when sparked in the usual way in a eudiometer over mercury, although the presence of moisture, or of any gas containing hydrogen, at once renders the mixture explosive. About the same time Berthelot found a rate of 1089 metres per second only for the propagation of the explosion wave through a theoretical mixture of the two gases ($2CO+O_2$) instead of the 1940 metres per second predicted by his formula, and he concluded that carbonic oxide is, so as to speak, ‘ a law unto itself.’ When, however, he found that a mixture of equal volumes of carbonic oxide, hydrogen and oxygen ($CO+H_2+O_2$) has a rate of 2008, compared with the 2236 metres per second predicted by his formula, he suggested that the hydrogen communicates to the carbonic oxide a law of detonation analogous to its own, which in view of recent work seems in a certain sense, although different from that which he meant, to be the truth.

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* *Trans. Chem. Soc.* 69 (1896), p. 759.

Dixon made a series of determinations with $2CO + O_2$ mixtures under different hygroscopic conditions between ‘ well-dried ’ gases (by means of strong sulphuric acid *plus* phosphoric anhydride) and mixtures saturated with steam at 75° C. He found the rate of explosion increased with the moisture content of the mixture up to ‘ saturation ’ at 35° C. (*i.e.* steam—5·6 per cent. by volume), after which it diminished as the moisture content was further increased, as follows :

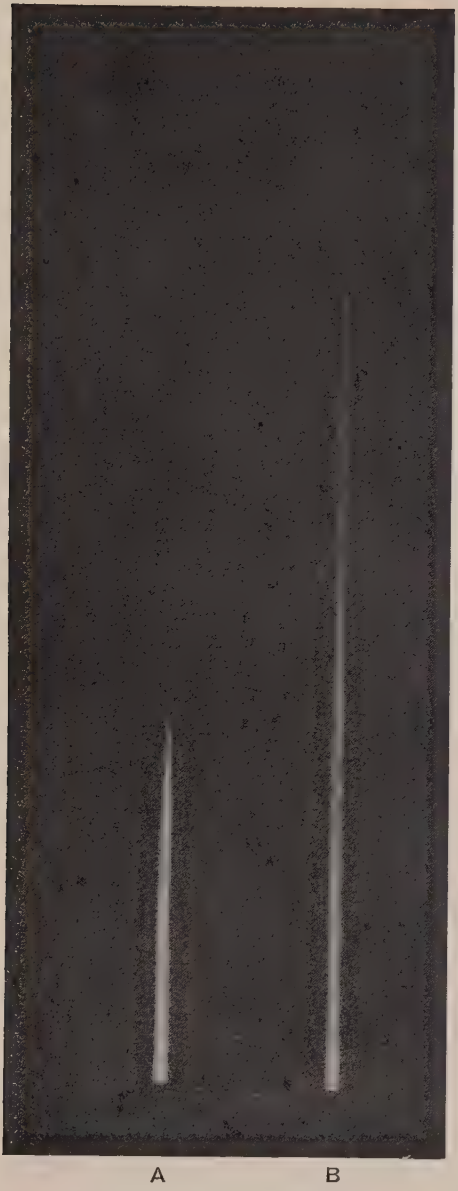
TABLE XLIII.—VARIATIONS IN THE RATE OF EXPLOSION OF A $2CO + O_2$ MIXTURE AT ATMOSPHERIC PRESSURE ACCORDING TO ITS HYGROSCOPIC CONDITION (DIXON)

Condition.	Per cent. Steam Present.	Rate in Metres per sec.
Well dried (conc. $H_2SO_4 + P_2O_5$)	—	1264
Dried (conc. H_2SO_4)	—	1305
Saturated at 10° C.	1·2	1676
,, ,, 20° C.	2·3	1703
,, ,, 28° C.	3·7	1713
,, ,, 35° C.	5·6	1738 *maximum*
,, ,, 45° C.	9·5	1693
,, ,, 55° C.	15·6	1666
,, ,, 65° C.	24·9	1526
,, ,, 75° C.	38·4	1266

The fact that Dixon found a rate of 1264 metres per second for a ‘ well-dried ’ mixture suggests that Berthelot’s very low value of 1089 metres per second may possibly have been due in part to the explosion wave not having been set up by the time the flame reached the first ‘ bridge ’ in his apparatus, whereas it was in Dixon’s experiments, where a longer preliminary run was allowed between the point of ignition and the first bridge.

In Plate XIX are reproduced two interesting photographs taken by Dixon in conjunction with Strange and Graham on a moving film, by means of similar apparatus to that already described on p. 167, of the explosion flames of (A) a “ moist ” and (B) a “ dried ” $2CO + O_2$ mixture, in each case dashing past a window in a detonating-coil. It will be seen that the image of the flame from the “ dried ” mixture is much more drawn out than that from the “ moist ” mixture, a circumstance which betokens a much slower combustion in the former case.

PLATE XIX.



A. The Explosion of 'Moist' Carbonic Oxide and Oxygen.
B. The Explosion of 'Dried' Carbonic Oxide and Oxygen.

Rates for Various Hydrocarbon-Oxygen Mixtures

The following rates for mixtures of one or other of the hydrocarbons methane, ethylene, and acetylene with varying proportions of oxygen are most instructive, especially in view of the rediscovery in Dixon's laboratory in the year 1891 of the fact, first observed by Dalton more than eighty years before, that an equimolecular mixture of ethylene and oxygen yields on explosion mainly carbonic oxide and hydrogen, as also does an equimolecular mixture of acetylene and oxygen. They shewed conclusively (i) that there are distinct stages in the combustion of hydrocarbons in explosions, the first alone being concerned in the propagation of the explosion wave, and (ii) *that in the wave* the carbon burns primarily to carbonic oxide, which in turn burns to carbonic anhydride in the rear of the wave. The rate of explosion for a mixture containing sufficient oxygen for *complete* combustion is always much less than the rate for one containing only sufficient oxygen to burn the carbon to carbonic oxide. The further discussion of the mechanism of hydrocarbon combustion must, however, be deferred until a later chapter, when it will be fully dealt with in the light of more recent work.

(*a*) *Methane-Oxygen Mixtures at* 10° C. *and* 760 *mm.*

Mixture -	$CH_4 + O_2$	$CH_4 + 1\frac{1}{2}O_2$	$CH_4 + 2O_2$
Rate - -	2528	2470	2322 metres per sec.

(*b*) *Ethylene-Oxygen Mixtures at* 10° C. *and* 760 *mm.*

Mixture -	$C_2H_4 + O_2$	$C_2H_4 + 2O_2$	$C_2H_4 + 3O_2$
Rate - -	2507	2581	2368 metres per sec.

(*c*) *Acetylene-Oxygen Mixtures at* 10° C. *and* 760 *mm.*

Mixture -	$C_2H_2 + O_2$	$C_2H_2 + 1\frac{1}{2}O_2$	$C_2H_2 + 2\frac{1}{2}O_2$
Rate - -	2961	2716	2391 metres per sec.

That the *whole* of the oxygen required for completely burning a hydrocarbon to carbon dioxide and steam is not active in the wave, is evident from the three following series of rates, namely :

Mixture -	$CH_4 + 1\frac{1}{2}O_2$	$CH_4 + 2O_2$	$CH_4 + 1\frac{1}{2}O_2 + \frac{1}{2}N_2$
Rate - -	2470	2322	2349 metres per sec.

Mixture -	$C_2H_4 + 2O_2$	$C_2H_4 + 3O_2$	$C_2H_4 + 2O_2 + N_2$
Rate - -	2581	2368	2413 metres per sec.

Mixture -	$C_2H_2 + 1\frac{1}{2}O_2$	$C_2H_2 + 2\frac{1}{2}O_2$	$C_2H_2 + 1\frac{1}{2}O_2 + N_2$
Rate - -	2716	2391	2414 metres per sec.

In each case the replacement of the last portion of the oxygen in the 'theoretical' mixture by its equivalent of nitrogen actually increases the rate of explosion, a circumstance which can have no other meaning than that the oxygen so replaced was *inert* in the wave, and retarded its velocity rather more than did the nitrogen which replaced it, because of its somewhat greater density.

Theories of the Explosion Wave

In 1893 H. B. Dixon adopted Berthelot's 'sound wave' theory *in principle*; but, finding that in many cases the rates predicted by the original formula were not in agreement with those actually observed, he modified it in the following particulars, namely: by assuming (i) that the explosion wave is carried forward by movements of molecules of density intermediate between that of the products of combustion and that of the unburnt gases; (ii) that the gases are heated *at constant volume*, and not, as Berthelot had supposed, at constant pressure; (iii) that each layer of gas is raised in temperature before being burnt, and that the temperature of the gas propagating the wave is double that due to the chemical reaction alone; (iv) that the temperature is increased when the chemical volume of the products is larger, and diminished when it is smaller, than that of the unburnt gases; and (v) that the velocity of a sound wave is only 0·7 of the mean velocity of the molecules in the gas. Dixon's modified formula was as follows:

$$V=0{\cdot}7\times 29{\cdot}354\sqrt{\frac{2\left(\frac{Q}{C_v}+t\right)\left(\frac{v_2}{v_1}\right)^{\gamma-1}}{d}},$$

where Q = the heat developed by the reaction, v_2 and v_1 = the chemical volumes of the products and unburnt gases respectively, d = the mean density of the products and the unburnt gases, and C_v = the specific heat of the products at constant volume (which, at that time, Dixon wrongly assumed to be independent of temperature), t = the initial temperature in °C., and γ = the ratio of the specific heats.

It was soon found, however, that, whereas in many cases the values of V calculated by this formula do agree with those actually found (*e.g.* for cyanogen-oxygen mixtures, and in nearly all cases where the detonating mixture is largely diluted with an inert gas), there are a number of cases, *e.g.* undiluted detonating mixtures, where the agreement is not good. Thus, whereas the calculated value for undiluted electrolytic gas—($2H_2+O_2$)—is 3416, the observed value is only 2820 metres per second. In 1893 Dixon ascribed such discrepancy to the partial dissociation of steam in the wave; but nowadays it seems doubtful whether such dissociation is anything like sufficient to account for it. In course of time it became recognised that the 'sound-wave theory' of the explosion wave, although at one time a useful working hypothesis, is fundamentally defective, and accordingly it has been superseded by a better. In 1910

Dixon himself wrote: "I do not believe to-day in the truth of my working hypothesis of the explosion-wave. It embodied a number of assumptions, some of which I have myself shewn to be erroneous. The theory of the explosion wave is not to-day dependent on the hypothesis of Berthelot and myself," * and he expressed his conversion to newer views developed independently by D. L. Chapman in 1899 and Jouguet in 1906, which now demand attention.

As far back as 1893 A. Schuster † had doubted the 'sound wave' theory, and drawn attention to the possibility of applying to the explosion wave Riemann's equation ‡ for the propagation of an abrupt variation in density and pressure through an inert gaseous medium, namely:

$$v=\sqrt{\frac{p-p_0}{d-d_0}\cdot\frac{d}{d_0}},$$

where p_0 and d_0 denote the pressure and density, respectively, of the medium through which the wave is travelling, and p and d denote respectively the maximum pressure and density developed at any point in the wave.

In 1899 D. L. Chapman, following up this suggestion, deduced from Riemann's equation a formula for rates of explosion, on the assumption that an abrupt variation in density and pressure can be propagated through a gaseous medium without change of type.

According to this view the explosion wave is to be regarded as a wave of compression not in a homogeneous medium but in a medium which is discontinuous in the vicinity of the wave-front. It is assumed (1) that the 'front' of the wave (*i.e.* from the unexploded gas to the point of maximum pressure) does not alter in character, or, in other words, that every portion of the wave travels with the same velocity; (2) that the velocity is the minimum velocity consistent with (1); and (3) that at the point of maximum pressure the chemical change concerned in the propagation of the wave is complete. The unburnt gases immediately in front of the waves are, of course, fired by compression, and the abrupt variation in the density and pressure of the medium is due to the chemical change. Chapman's formula for the velocity of the explosion wave in centimetres per second is

$$V=\sqrt{\frac{2RJ}{\mu C_v^2}[\{(m-n)C_p+mC_v\}C_pt_0+(C_p+C_v)h]},$$

where R = the gas constant (1·985), J = the dynamical equivalent of heat (42×10^6 ergs), μ = the gram equivalents of the mixture exploded (*e.g.* 58 in the case of $C_2H_2+O_2$), n and m = the number of gaseous molecules before and after the chemical change in the wave, C_p and C_v = the mean specific heats of the products at constant pressure and volume respectively,

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* *Trans. Chem. Soc.* **97** (1910), p. 665.

† *Phil. Trans.* A. **184** (1893), p. 152.

‡ See Rayleigh's *Theory of Sound*, 1896, or Lamb's *Dynamical Theory of Sound*, 1925.

h = the total heat generated in the wave, and t_0 = the initial temperature (abs.) of the mixture exploded. From the fact that the dilution of electrolytic gas ($2H_2+O_2$) with oxygen lowers its rate of explosion a little more than a corresponding dilution with nitrogen, Chapman considers it improbable that there is any appreciable dissociation of steam in the wave. He assumed that the molecular heat of steam rises more rapidly with temperature than that of a diatomic gas, and that the molecular heats of oxygen, hydrogen, nitrogen, and carbon monoxide may for all practical purposes be considered as equal at any given temperature. Selecting some seventeen of Dixon's found rates of explosion he calculated by means of his formula the corresponding molecular heats and temperatures, arriving at the following results for C_v at intermediate temperatures by interpolation :

	Temperature -	4,300°	4,000°	3,700°	3,400°	3,100°	2,800°	2,500°
C_v	Steam - -	14·750	14·297	13·750	13·102	12·250	11·040	9·797
	Diatomic gases	7·707	7·674	7·641	7·608	7·575	7·542	7·509

With the aid of this series of numbers he proceeeded to apply his formula to the calculations of the rates of explosions of some forty other mixtures investigated by Dixon, finding in all cases close agreement between the found and calculated values, of which the following may suffice as examples :

Table XLIV.—Calculated Rates of Detonation (Chapman)

Mixture Exploded.	Products in the Wave.	Temperature.	Rate of Explosion. Metres per Second.	
			Calculated.	Found.
$2H_2+2N_2O$	$2H_2O+2N_2$	3813°	2408	2305
$4H_2+2N_2O$	$2H_2O+2N_2+2H_2$	3077°	2604	2545
$6H_2+2N_2O$	$2H_2O+2N_2+4H_2$	2612°	2720	2705
$2H_2+2N_2O+2N_2$	$2H_2O+4N_2$	3077°	2097	1991
$C_2H_4+2O_2$	$2CO+2H_2O$	4365°	2619	2581
$C_2H_4+3O_2$	$2CO+2H_2O+O_2$	3882°	2348	2368
$C_2H_2+O_2$	$2CO+H_2$	5029°	3101	2961
CH_4+O_2	$CO+H_2O+H_2$	2772°	2502	2528
$2CH_4+3O_2$	$2CO+4H_2O$	3764°	2485	2470
$2CH_4+3O_2+N_2$	$2CO+4H_2O+N_2$	3513°	2353	2349

It was soon recognised that Chapman's formula affords a ready explanation of the fact already referred to, that when electrolytic gas is diluted with excess of hydrogen the rate of explosion progressively increases, whereas dilution with either nitrogen or excess oxygen has the opposite effect. For if the formula be written as follows :

$$V^2 = \frac{2RJ}{\mu C_v^2}[\{(m-n)C_p + mC_v\}C_p t_0 + (C_p + C_v)h],$$

and putting $\frac{2RJ}{\mu C_v^2}=A$, and the terms between the square brackets $=B$, it will be immediately perceived that the addition of an inert diatomic gas (*e.g.* H_2, N_2, or O_2) to a given explosive mixture will affect the values of both A and B, but not necessarily in the same direction. It will increase the value of μ and diminish the values of C_v and C_p, partly by lowering the temperature in the wave and partly also (if steam or carbon dioxide be formed in the wave) by reason of its own specific heat being lower than that of the undiluted products. It will also increase the value of m without altering $(m-n)$. If it be assumed that the molecular heats of the three diatomic gases under consideration are, for all practical purposes, equal at any given temperature, it will be at once seen that an equal dilution of a given explosive mixture with any one of the three gases, whilst it will have an equal effect on all terms included under B, may either increase or diminish the value of A, according as to whether or not the plus effect of the lower value of C_v is counterbalanced by the minus effect of the increase in μ. If the latter effect be small, as would be the case with hydrogen as diluent, the value of A would on the whole be increased; whereas, if the increase in μ were large, as would be the case with nitrogen or oxygen as the diluent, the value of A would on the whole be diminished.

As an example of the probable effects of the equal dilution of a given explosive mixture with each of the three gases in question the case of an equimolecular mixture of hydrogen and nitrogen oxide, fired at 10° and 760 mm., may be cited as follows:

TABLE XLV.—CALCULATED RATES OF DETONATION SHEWING INFLUENCE OF DILUENT GAS (CHAPMAN)

Mixture.	h.	m.	$m-n$	μ.	C_v.	Temp.	A.	B.	V in Metres per second.	
									Calculated.	Found.
H_2+N_2O	152,500	4	0	92	10·81	3813°	15,640	3,758,750	2408	2305
$H_2+N_2O+2H_2$		6	0	96	9·10	3077°	20,980	3,251,500	2612	2545
$H_2+N_2O+2N_2$		6	0	148	9·10	3077°	13,610	3,251,500	2097	1991
$H_2+N_2O+2O_2$		6	0	156	9·10	3077°	12,830	3,251,500	2042	—

An inspection of the figures under A and B will at once make it clear why dilution of such a mixture with excess hydrogen has the opposite effect upon its rate of explosion to an equal dilution with either nitrogen or excess oxygen.

In the same year that Chapman published his formula, Vieille * made a series of experimental determinations of the velocities of the 'shock waves' ('*l'ondes de choc*') set up in a glass tube full of air or other gases, by either the bursting of a celluloid diaphragm under pressure or the explosion of a charge of mercury fulminate at one end of it. The results of his experiments shewed that the velocities of such 'shock waves' for some distances from their origin are much greater than that of sound through the same medium, although on continued propagation the 'shock wave' gradually loses its extra energy and eventually would doubtless become an ordinary sound wave. He formed the opinion that probably the propagation of a 'detonation wave' through a gaseous explosive medium is a parallel phenomenon; such a wave, being essentially a 'shock wave,' has its *abrupt* change in pressure in the vicinity of the wave front maintained by the adiabatic combustion of the explosive medium through which it is propagated. In this connection he wrote:

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* *Mem. de poudres et saltpetres*, 10 (1899), p. 177; *Compt. Rend.* 131 (1900), p. 413.

"*Les phénomènes de discontinuité paraissent jouer un rôle fondamental dans le mécanisime de la detonation des mélanges explosifs; les vitesses considérables observées sur ces mélanges se trouvent ramenées en effet aux vitesses de propagation d'une discontinuité dans un milieu inerte, mais avec cette condition particulière que la discontinuité est entretenue sans amortissement par la reaction chimique provoquée au passage de l'onde en raison d'une loi spéciale de compression adiabatique dynamique dont Hugoniot a donne l'expression remarquable.*"

Indeed, Vieille found that his 'shock wave' velocities were in agreement with those calculated by means of the following formula, which had been deduced in accordance with Hugoniot's theory,* namely:

$$V=\sqrt{\frac{p_0}{d_0}\left(\gamma+\frac{\gamma+1}{2}\times\frac{p_1-p_0}{p_0}\right)},$$

where p_0 and d_0 denote the initial pressure and density respectively of the medium, p_1 the pressure in the wave, and γ the ratio of the specific heats at constant pressure and volume respectively. This equation, whilst analogous to that of Riemann, is based upon the assumption that the medium through which the 'shock wave' is travelling has a changed elasticity ('*l'élasticité adiabatique dynamique*') in its path.

In 1905–6 E. Jouguet,† who was apparently unaware of Chapman's earlier work, applied Hugoniot's theory to the explosion wave, and after an exhaustive mathematical study of the subject he deduced the following formula:

$$\left(\frac{dp}{dt}\right)^2 \text{ i.e. } V^2=\mu^2\frac{RnT}{M}\left(1+\frac{nR}{MC_v}\right),$$

in which:

μ = the ratio of the densities of the medium *after* and *before* the wave front;

R = the gas constant;

T = maximum temperature in the wave;

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* *Journ. de Math. pure et appl.* (4), 3 (1887), p. 477, and (4) 4 (1888), p. 153.

† *Journ. de Mathématiques*, 1905 and 1906; see also *Mechanique des Explosifs*, Paris, 1917.

n=the number of gram-molecules in the explosion products;
C_v=the mean specific heat at constant volume of the explosion products;
M=the molecular mass of the gaseous medium.

In applying the formula it should be borne in mind that it is the chemical change *in the wave itself*, and no other, which determines its velocity.

From the many values which Jouguet calculated the following may be cited and in certain cases compared with those deduced by Chapman (Table XLIV.).

TABLE XLVI.—CALCULATED RATES OF DETONATION (JOUGUET)

Mixture.	M Grams.	μ.	Calorific Power ML (Large Cals.).	$\frac{P_2}{P_1}$.	Max. Temp. °C.	Rate of Explosion.	
						Calculated.	Found. Dixon.
$2H_2+O_2$	18	1·879	58	17·5	3956°	2629	2821
$2H_2+O_2+5H_2$	23	1·79	58	14·4	2596°	3526	3530
$2H_2+O_2+5N_2$	88	1·79	58	14·4	2596°	1798	1822
$2H_2+O_2+5O_2$	98	1·79	58	14·4	2596°	1692	1707
$2H_2+2N_2O$	46	1·865	79·6	25·9	3933°	2350	2305
$C_2H_2+O_2$	58	1·84	113	54·5	5570°	3091	2961
H_2+Cl_2	36·5	1·787	22	24·5	3880°	1851	1729

In calculating the maximum temperatures reached in the wave Jouguet used the mean specific heat values deduced by Mallard and Le Chatelier, though he realised that they might not be of great accuracy at the highest temperatures. Moreover, like Chapman, he considered that dissociation would not play any great part during the propagation of the detonation wave in the explosive mixtures quoted above, yet he thought the possibility of its interference an objection to his deductions.

In a recent paper Jouguet * has published a comparison between the rates of explosion calculated by means of his formula, using mean specific heats calculated on Kast's formula (based on Pier and Bjerrum's work), and those determined experimentally, making allowances for possible dissociation. He found that the occurrence of dissociation would modify the results little—tending to lower the calculated speeds very slightly. Using Kast's formula the calculated detonation speeds for hydrogen-oxygen mixtures were now higher than the experimental values. In this connection he said: "*Les grands valeurs de* T_2 (temperature in the wave) *montrent que le calcul exige une extrapolation très grande, donc très uncertaine, des lois de la dissociation et des chaleurs spécifiques. Pour les chaleurs spécifiques notamment, on sait bien aujourd'hui que les formules de Mallard*

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* *Comptes rendus*, 151 (1925), p. 546.

et Le Chatelier les font croître trop rapidement avec la température. Il est permit de se demander, si celles de Kast ne les font pas, au contraire, croître trop lentement. . . ."

Recent Experimental Work

Although nothing much of outstanding importance concerning the explosion wave has been discovered experimentally since Dixon's classical work, there are a few new matters which should be referred to before leaving the subject.

In the year 1914 H. B. Dixon, in conjunction with C. Campbell and W. E. Slater,* published an account of some experiments in which they had exploded certain mixtures of (i) cyanogen with oxygen and nitrogen in varying proportions, (ii) hydrogen and oxygen, (iii) acetylene and oxygen, (iv) carbon disulphide and oxygen, and (v) carbonic oxide and oxygen, both in a magnetic field of 10,000 gauss and without it, and had analysed photographically in each case the resulting explosion wave. They were, however, unable to detect any visible effect produced in any of the explosions by the magnetic field employed, from which they concluded that " there appears to be no ground for assuming that the velocity of the explosion wave is due to the ionising action of electrons." It may be doubted, however, whether the magnetic field which they employed was sufficiently powerful for the purpose ; and too much weight should not be given to the negative result of such an experiment.

In recent years C. Campbell † has studied the effects of abrupt changes in diameter of the containing vessels (tubes) upon detonation waves developed in various explosive gaseous media ; the wave velocity was only affected appreciably, however, in passing abruptly from a narrower to a wider tube, when the wave was damped down. More recently it has been demonstrated by Laffitte ‡ that in such circumstances the flame is re-established as a true detonation wave after it has traversed a certain distance (dependent on the nature of the mixture, and the relative diameters of the tube), where it was damped down. Thus it was found that the distances required for the re-establishment of detonation waves, after they had been damped down by passage from a tube of 7 mm. diameter into one of stated greater diameter, were as follows :

Diameter of wider tube - - -		13	16	23	33	43 mm.
Distance for	CS_2+3O_2 *mixture* -	8	10	15	50	100 cms.
	$2H_2+O_2$ *mixture* -	—	—	3	62	—

Laffitte § has also measured photographically the distances traversed by the flame before a true detonation wave is established when a CS_2+3O_2

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* *Proc. Roy. Soc.* A. **90** (1914), p. 506.

† *Proc. Roy. Soc.* A. **121** (1922), p. 2483.

‡ *Comptes rendus,* **179** (1924), p. 1394.

§ *Comptes rendus* **176** (1923), p. 1392.

mixture is fired by spark at the closed ends of tubes of varying diameter—and has given the following figures :

Diameter of Tube. mm.	Distance traversed by Flame prior to Detonation. cm.
6·5 – 7	48
10	50
24 – 25	58
34 – 35	84
43 – 44	103
53 – 54	121

More recently he has published with P. Dumanois * the following figures showing the effect of the initial pressure of a $2H_2 + O_2$ mixture upon such pre-detonation distances in a 22 mm. tube.

Initial Pressure (Atmospheres).	Distance traversed by Flame prior to Detonation. cms.
1	70
2	60
3	52
4	44
5	35
6	30
6·5	27

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* *Loc. cit.* 183 (1926), p. 284.

CHAPTER XVII

STATIONARY FLAMES AND THEIR STRUCTURE

So far we have considered moving flames as they are propagated through homogeneous explosive mixtures. Most people, however, are probably more familiar with stationary flames, *e.g.* those of hydrocarbons or coal-gas, as ordinarily used in everyday life for lighting and heating purposes. In these a jet of gas or vapour, with or without admixture of air, is ignited as it issues from the orifice of a ‘ burner,’ where it burns steadily without changing its form or position so long as no alteration is made in the gas (or gas-air mixture) supply. Outwardly there appears to be a great difference between such stationary flames and moving ones; on closer examination, however, the apparent differences are found to be mainly in degree rather than in kind, because in both cases the flame is due to the combustion of an explosive mixture of combustible gas or vapour and air.

There is, however, one important difference in condition between the two cases which should be noticed, because it is reflected in structural differences. In the cases considered so far flame is propagated through an explosive medium which is homogeneous, and the structure of the travelling flame, whether differentiated or not, is determined accordingly. But when a jet of combustible gas, or of gas mixed with less air than is required for complete combustion, issues from the burner orifice, it immediately begins to mingle with the surrounding air, forming with it a series of mixtures whose compositions vary from layer to layer, and when these mixtures are ignited at any point the resulting flame preserves the heterogeneous condition and acquires a structure accordingly.

Now, for a steady stationary flame to be maintained at or near the orifice of the burner a certain condition must be fulfilled, namely, that in each of the successive layers of explosive mixtures the upward flow of ignitible gas and air mixture has a velocity just balancing that at which flame is propagated downwards through it under the conditions prevailing. In this connection it should be borne in mind always that conditions of high, though very varying, temperature prevail in all regions of the flame.

Luminous Flames

In his writings on flame Humphry Davy gave the following description of an ordinary luminous flame: "The form of flame is conical, because the greatest heat is in the centre of the explosive mixture. In looking steadfastly at flame, the part where combustible matter is volatilised is seen, and it appears dark, contrasted with the part in which it begins to burn, that is where it is so mixed with air as to become explosive. This heat diminishes towards the top of the flame, because in this part the quantity of oxygen is least."

Berzelius appears to have been the first to describe an ordinary candle flame as consisting of four distinct zones. His description, which can hardly be improved upon, is given on page 22 of the 1822 English edition of his book on *The Use of the Blowpipe*, as follows: "If we attentively consider the flame of a candle we may remark several unequal divisions of it, of which four may be distinguished. We see at its base a small part of a dark blue colour, which becomes thinner as it gets farther from the wick, and disappears entirely where the external surface of the flame ascends perpendicularly. In the middle of the flame is a dark space seen through its brilliant covering. This space encloses the gases which issue from the wick, which, not being yet in contact with the air, cannot undergo combustion. Round this space is the brilliant part of the flame, properly so called, and, lastly, beyond this we may perceive, by attentive inspection, the outer covering of all, slightly luminous, and whose greatest thickness corresponds with the summit of the brilliant flame. It is in this outer part that the combustion of gases is completed and the heat the most intense."

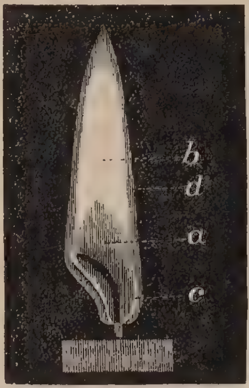

FIG. 80.—STRUCTURE OF A CANDLE FLAME.

Although more than one observer during the first half of last century attempted to add to the four parts or zones of a luminous flame distinguished by Berzelius, his number is still retained by general agreement amongst chemists. We therefore distinguish (see Fig. 80):

(1) *A dark-blue region at the base* (*c*), which is generally regarded as a region of immediate complete combustion, because sufficient air is present to burn the hydrocarbons completely without any separation of carbon.

(2) *An innermost dark region* (*a*), which, as Francis Bacon observed, is really hollow, being a region where no combustion occurs but only combustible gases and vapours are ascending.

(3) *A middle luminous region* (*b*), where partial combustion occurs and

carbon is deposited, which being raised to incandescence by the heat of the flame causes its luminosity, as Davy rightly said.

(4) *A faintly-luminous mantle* (*d*), ensheathing the whole, where the products of partial combustion from (3) are finally burnt.

As will be seen in a later chapter, when the question of the combustion of hydrocarbons and separation of carbon in flame is discussed, there is no longer any material differences of opinion amongst chemists that the luminosity of the flame is due to the separation of solid carbon in its middle luminous region, although in the past there have been considerable controversies about it. It may be recalled how in 1868 E. Frankland * showed that flames containing only gaseous matter, and in which no solid carbon could be separated, become luminous under pressure, from which he concluded that the luminosity of ordinary flames is due to the incandescent vapour of dense hydrocarbon. Since then, however, Stokes and Burch shewed that, by focussing the image of the sun on to the flame, and examining the scattered light with a Nicol prism, it is polarised, thus proving conclusively that the flame contains *solid* particles.

In Fig. 81, Plate XX., is reproduced a beautiful photograph by A. Smithells of a flat flame of coal-gas viewed edgewise shewing the various zones; the blue burning sheath encloses the dark zone of unburnt gas at the bottom and the luminous zone at the top.

The Bunsen Flame

In an ordinary Bunsen burner the gas issuing under pressure from the two minute orifices in the nipple near the base draws in (' injector-wise ') a certain proportion of ' primary ' air through the open ports on opposite sides of the jet; the areas of the ports can be varied from 0 to ' full open ' as circumstances require. With the gas ' full on,' at say 3 inches water-gauge pressure, and the ports ' full open,' the injector-action of an ordinary Bunsen burner produces in the tube an explosive mixture of (say) one volume of coal-gas with from 2 to 2½ volumes of ' primary ' air, or about half that required for complete combustion. This mixture, after ascending the tube of the burner, issues at the top with a certain steady velocity which, in order to prevent ' back-firing,' must not be less than that at which flame would be propagated downwards through the mixture. On ignition the familiar feebly luminous two-coned Bunsen flame is produced, in which usually no carbon separates.

The inner blue cone (Fig. 82, Plate XX.), is a region of incomplete combustion, where the constituents of the coal-gas are partially burnt, by the defective oxygen supply contained in the ' primary ' air, with the production of oxides of carbon, steam, hydrogen, and nitrogen, which, passing onwards into the outer cone, undergo complete combustion there.

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* *Proc. Roy. Soc.* 16 (1868), p. 419.

PLATE XX.

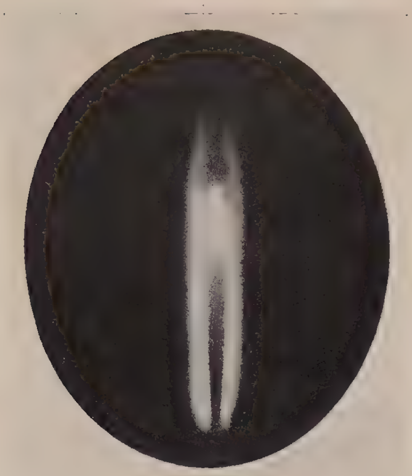

FIG. 81.—FLAT LUMINOUS COAL-GAS FLAME VIEWED EDGEWISE. (Smithells.)
(From the *Transactions of the Institution of Gas Engineers.*)

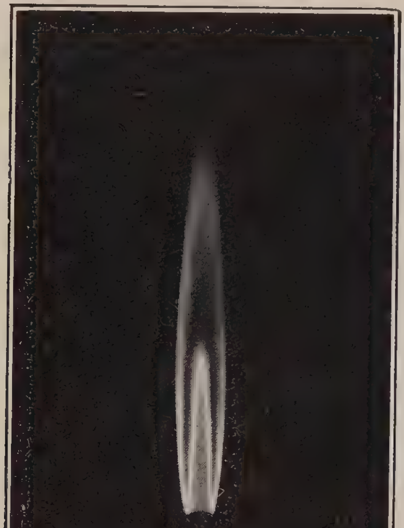

FIG. 82.—BUNSEN FLAME.

The Méker Burner

The Méker burner (Fig. 83) is a modern development of the 'Bunsen,' being so constructed that the 'primary' air supply taken in is practically sufficient for complete combustion. The explosive gas-air mixture passes out of the expanded head of the burner through a deep metal grid, and is ignited as it issues therefrom. The result is a very hot single-cone 'solid' flame of minimum volume.

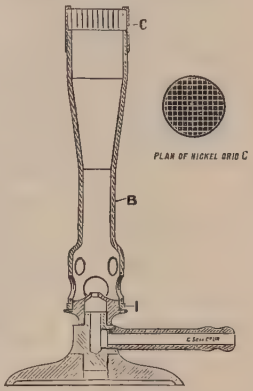

FIG. 83.—MÉKER BURNER. (From Thorpe's *Dictionary of Applied Chemistry*.)

The Teclu and Smithells' Flame-Separators

Up to about the year 1890, the general view taken of the Bunsen flame seems to have been that it is a mass of burning gas with an inside surface (the inner-cone) and an outside surface (the other cone) between which the gas undergoes a progressive combustion, and such may be largely true if the 'primary' air supply is much restricted. The essentially dual character of the flame, as comprising a partial combustion in the inner cone which is completed in the outer one, was not then generally recognised.

In the years 1891–2, however, two papers of outstanding importance appeared which put things in a new light, and gave us our modern conception of the flame structure. One was by an Austrian chemist, N. Teclu, the designer of the burner known by his name, and the other by A. Smithells and H. Ingle in this country. It was one of the many cases in the history of science when two investigators working simultaneously upon the same problem, but quite independently and unknown to each other, happen upon a similar line of attack, and to a certain extent overlap in their discoveries.

Teclu's Experiments

Teclu [*] made and described experiments which shewed (to quote his own words): "*Dass eine Leuchtgasflamme durch Zutritt von Sauerstoff aus der atmosphärischen Luft unter geeigneten Umständen sich in zwei Flammen spalten kann, von denen die eine an ihrer ursprünglichen Stelle fortbrennt, während die andere in Bewegung nach abwärts gelangt*," together with an apparatus to effect such results.

In the illustration of the apparatus (Fig. 84) *A* represents a glass tube 60 cm. long and 2 cm. diameter, open at the top but closed at the bottom by a cork with a central hole through which the stem of an inverted filter funnel *B* (8 cm. diameter) was inserted as shewn. A supply of coal-gas was delivered through a glass tube *C* (3 mm. diameter), bent as in the diagram, near the exit of which a bulb was blown of a size sufficient to block the stem-opening of *B* if thrust up against it. In making an experiment a current of gas was turned on through *C*, the upper end of which was then thrust into the stem-opening of *B*, and the gas then lighted as it issued from the top of *A*. By subsequent careful adjustment of the position of the bulb on *C*, relative to the stem-opening *B*, a regulated 'primary' air supply could be admitted with the stream of gas entering the bottom of *A*. As the 'primary' air supply was gradually increased the flame at the top of *A* first lost its luminosity, then developed the familiar two-cone 'Bunsen'-flame structure, until finally the inner cone began to detach itself and descend *A*, leaving the outer cone still burning in its original position at the top thereof. By such means a flame "*welche in allen ihren Eigenschaften der Flamme des Bunsen'schen Brenners entspricht*" was produced, and its two cones separated.

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[*] *Jour. prak. Chem.* **44** (1891), pp. 246–255.

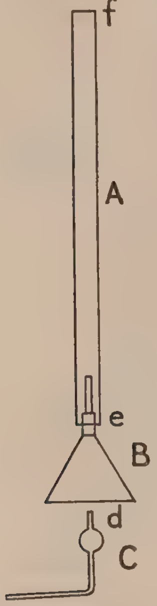

Fig. 84.—Teclu's Apparatus.

Moreover, as Teclu said: "*Man kann in diesem Falle deutlich beobachten, dass die bläuliche, kaum heiss zu nennende obere Flamme mit ihrer Brandfläche nach oben gekehrt ist, und somit die an derselben vorsichgehende Verbrennung den Sauerstoff aus der umgebenden Luft entnimmt, während die untere, grünlich gefärbte, sehr heisse Flamme in der Röhre mit ihrer Brandfläche nach unten gewendet erscheint, und die hier stattfindende Verbrennung sich durch den Sauerstoff der Luft Vollzeiht, welcher, dem Leuchtgase beigemengt, den Apparat durchströmt.*"

Such then were the essential features of Teclu's experimental contribution to the subject; it should be observed that (1) he worked with coal-gas only, and (2) made no attempt to analyse the interconal gases produced in his apparatus. Nor did he, so far as we know, subsequently follow up the matter scientifically further.

The burner which Teclu invented was based upon observations made during his investigation, and enabled the 'primary' air supply to be graduated with nicety. Because of this, Smithells employed it preferably to the older Bunsen burner as the one on which to mount his separator, and others have found it equally useful in other connections.

Smithells' Researches

Smithells and Ingle's experiments * were undertaken primarily with the object of enquiring into the chemistry and structure of hydrocarbon flames, it being hoped that, by employing single hydrocarbons of definite compositions, it would be possible to trace the chemical changes taking place in different regions of the flame with more accuracy and definiteness than is possible when using coal-gas, kerosene oil, etc., as previous investigators had done up till then. They started out from the well-known lecture experiment, in which a long vertical glass tube is fixed on to a Bunsen burner, so as to make a wider prolongation of its tube. In such a device, by either diminishing the gas supply or increasing that of the air after the flame has been lighted at the top of the extended tube, the ordinary two-coned flame structure can be developed; by further gradually diminishing the gas supply the inner cone becomes smaller and green in colour, until finally the flame travels down the glass tube, where, usually after a period of 'vibratory' motion, it either causes a sharp 'back-fire' to the bottom of the burner or goes out.

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* *Trans. Chem. Soc.* **61** (1892), pp. 204 to 216.

On repeating the experiment Smithells and Ingle found that if the relative proportions of gas and air were carefully adjusted until the flame would just, but only just, recede, it would pass down the glass tube for 12 inches or so and then return to the top. In this way an oscillation of the flame could be maintained continuously for two hours. On closely inspecting the apparatus in such condition it was found that the flame did not recede as a whole, but that it divided into two parts, namely, (1) an inner cone which became flatter and greener as it entered and descended the glass tube, and (2) a larger, scarcely luminous, lilac-coloured cone which remained in its original position at the top of the tube.

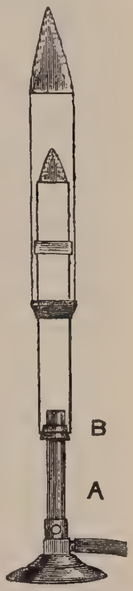


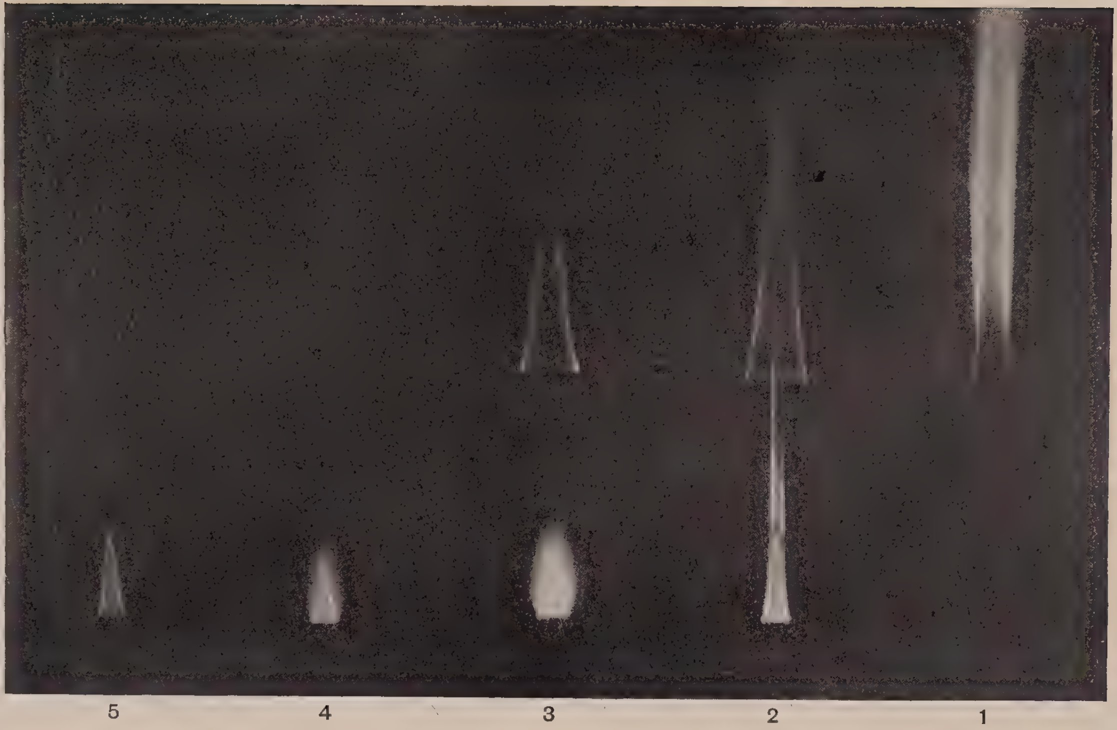
Fig. 85.—Smithells' Flame Separator.

From this observation they proceeded to devise their well-known 'flame separator,' which is shewn diagrammatically in Fig. 85. Although an ordinary Bunsen, or better still a Teclu burner, may be used for the supply of gas and air, it was found even more convenient to substitute for it a ⊥-piece at *A*, passing through a cork at *B*, so as to have the supplies of gas and air more completely under control. The upper part of the apparatus consists of two co-axial vertical tubes so arranged that, whilst having an air-tight joint between them, the outer one will slide freely over the other. If now the mouth of the inner tube be held about 10 cm. below that of the outer one, and a gas air mixture in suitable proportions be lighted as it issues at the top of the outer tube, an ordinary non-luminous two coned Bunsen flame can be obtained there. On gradually diminishing the gas supply, without altering that of the air, the flame becomes smaller, until the inner cone, having become very small and green in colour, shews a tendency to enter and pass down the tube. If then the gas supply be further diminished the inner cone will descend and re-ascend the wider tube a few times, until at length it descends as far as the mouth of the narrower tube, where it will suddenly settle and remain, whilst a feeble lilac-coloured flame remains at the mouth of the wider tube. Thus the two cones of the Bunsen flame may be separated, so that the composition of the inter-conal gases may be studied.

Although the original apparatus was made of glass it should nowadays be constructed preferably of quartz tubes, to avoid their cracking with the heat, as formerly they were very liable to do. The structure of hydrocarbon flames can best be studied by using with the apparatus a by-passed 'saturator' containing benzene instead of the usual coal-gas supply. For most ordinary purposes a wide glass tube containing a roll of flannel soaked with the hydrocarbon answers very well. Part of the air after passing through the saturator rejoins the main current, and passes into the apparatus, where, by suitable regulation, a non-luminous flame can be obtained, and separated into two cones.

In their original memoir Smithells and Ingle gave the following description, which may help readers to an understanding of the structure of hydrocarbon flames. "The appearances presented are, in the case of liquid hydrocarbons, not quite the same as with those which are ordinarily gaseous. As a rule, with the vapour of liquid hydrocarbons, a considerable degree of luminosity is maintained until the moment of descent of the inner cone, whereupon both cones become non-luminous. Besides this, the inner cone presents a peculiar appearance. It is divided by dark lines into several (usually five or six) petal-like segments, which often revolve with great rapidity round a vertical axis. Air charged with benzene vapour affords an example of this class of flame, and with it also two more points of special interest may be observed. If, after the two non-luminous cones have been separated, the supply of benzene-vapour be increased, a luminous tip appears in the inner cone, and on further increasing the benzene this tip extends as a vertical streak of separated carbon. It is luminous for some distance above the inner cone, then cools down, and only becomes incandescent again on passing through the tip of the upper cone. If the benzene supply be diminished the luminous streak disappears, the upper cone becomes smaller and smaller and finally disappears altogether. Meanwhile the inner cone has become smaller, and more vivid and hotter, and now the whole combustion is taking place in this single cone of flame. If more benzene be cut off the proportion of air becomes excessive, the flame cools, loses brilliance, and slightly enlarges. Finally, a further diminution of benzene causes the flame to rise from the inner tube, slowly pass upwards, and disappear." These appearances are shewn in Plate XXI., reproduced by permission from photographs originally published in Smithells and Ingle's paper, representing the gradual transition without

PLATE XXI.



Appearances of a Benzene Flame with Varied Aëration in a Separator. (Smithells and Ingle.)

even momentary extinction for a flame containing excess of hydrocarbon (1) to one containing excess of air (5).

Smithells and Ingle published the following analyses of the inter-conal gases yielded by the flames of various combustible gases :

TABLE XLVII.—COMPOSITION OF INTER-CONAL GASES FROM VARIOUS 'AËRATED' FLAMES (SMITHELLS AND INGLE)

Gas burnt.		Ethylene. C_2H_4.	Methane. CH_4.	Pentane. C_5H_{12}.	Heptane. C_7H_{16}.	Benzene. C_6H_6.	Coal-gas.
Diameter of outer tube in mm. - -		29	29	20	20	19	19·5
Diameter of inner tube in mm. - -		20	20	13	13	8	12
Percentage composition of inter-conal gases	CO_2 -	3·6	6·8	7·0	6·5	13·1	4·2
	CO -	15·6	4·5	7·9	9·5	5·0	8·8
	Hydrocarbons	1·3	—	—	—	0·6	—
	H_2 -	9·4	3·9	5·4	5·8	0·64	9·3
	H_2O -	9·5	17·6	13·1	12·3	7·7	16·0
	N_2 -	60·6	67·2	66·2	65·6	73·1	62·0

In all cases the inter-conal gases were mainly composed of the two oxides of carbon, hydrogen, steam, together with nitrogen originating in the 'primary' air-supply. In the coal-gas experiment the mixture burning at the inner tube was 1 volume of coal-gas to about 4·8 volumes of air, or one containing about twice the amount of air usually admitted as the 'primary' supply in an ordinary Bunsen burner. In the case of benzene the mixture burnt was about 1 volume of vapour to about 30 of air.

It was thus shewn that in the inner cone of the Bunsen burner the combustible gases in question are partially burnt, producing a mixture of oxides of carbon, hydrogen and steam without separation of carbon, a conclusion which at the time was of outstanding interest, because it was diametrically opposed to the then prevailing doctrine of the preferential combustion of hydrogen in hydrocarbon flames.

In 1894 Smithells and Dent * published the results of their investigation of the cyanogen flame. They found that a cyanogen flame, burning at a small circular orifice, consists of (i) an inner region of a bright peach-blossom tint, enveloped by (ii) an outer cone of a colour between bright blue and greenish-grey. On burning the flame in a cone-separating apparatus, and gradually adding air, the inner cone became smaller, and eventually descended the outer tube. Separation of the two cones

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* *Trans. Chem. Soc.* 65 (1894), pp. 603–610.

just occurred when the ratio C_2N_2 to air in the mixture burnt was 1 : 3·3. During the process of detachment the inner cone was surrounded by a rosy halo, which adhered to it after the descent. On further increasing the air supply this rosy halo disappeared and was replaced by a blue one. The outer cone flame remained all the while at the mouth of the wider tube, retaining its original colour and appearance. Further addition of air caused an extinction of the outer cone, and simultaneously the inner one to take a bluer, and its halo a greener tint. The sequence of changes just described is depicted in the diagram (Fig. 86, *a*, *b*, *c*, *d*).

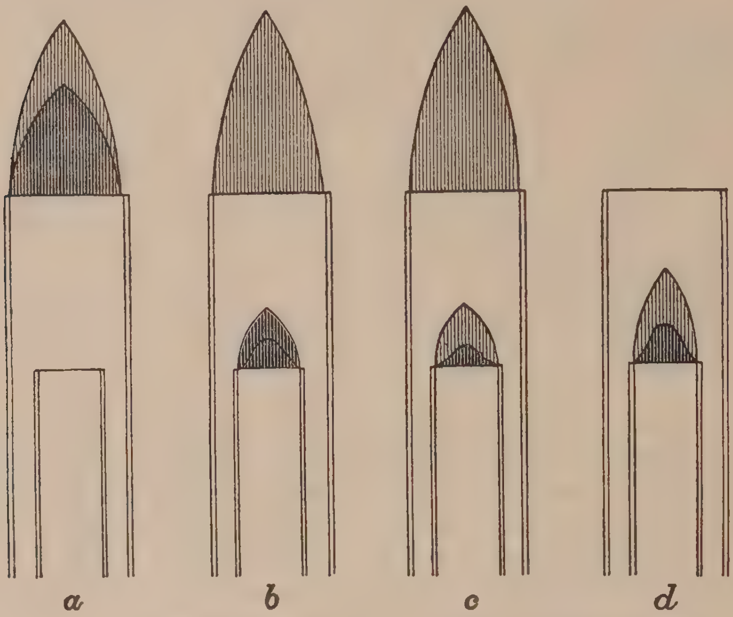

Fig. 86.—Illustrating Smithells and Dent's Experiment with an Aërated Cyanogen Flame.

Analyses were made of the inter-conal gases under varying operating conditions, with the results shewn in table :

Table XLVIII.—Percentage Composition of the Inter-conal Gases for an Aërated Cyanogen Flame (Smithells and Dent)

Ratio Air/C_2N_2	Rose-Coloured Halo.				No Halo.	Blue Halo.	
	3·31	3·56	4·02	4·06	5·57	6·02	6·74
C_2N_2 - -	7·4	6·1	4·3	3·8	0·1	*nil*	*nil*
CO_2 - -	0·5	0·8	1·4	1·5	4·7	5·8	8·6
CO - - -	25·5	25·4	25·2	24·4	22·0	19·9	15·3
N_2 - - -	65·8	66·9	68·5	69·2	73·3	74·3	75·2
N oxides -	0·8	0·7	0·6	1·1	*nil*	0·4	0·9

These results confirmed, and extended to the conditions of ordinary flames, the conclusion previously deduced by H. B. Dixon from his study of the 'rates of explosion' of cyanogen-oxygen mixtures (see p. 176, Chapter XVI), namely, that cyanogen burns in two distinct stages, namely:

(i) $C_2N_2 + O_2 = 2CO + N_2$,

and (ii) $2CO + N_2 + O_2 = 2CO_2 + N_2$.

Of these it was now shewn that (i) occurs principally in the inner cone, and (ii) in the outer cone. Also, evidence was forthcoming that there is no essential difference between the character and sequence of the chemical changes concerned in ordinary flames and in the explosion wave.

It would seem as though the 'rose-coloured halo' observed round the inner cone when the air-supply was very defective might have been due to the presence in it of highly-heated cyanogen, because it disappeared as soon as the amount of cyanogen in the inter-conal gases had become negligible; the 'blue-coloured halo' which succeeded it might be due to burning carbonic oxide; whilst the 'green' one might be due to oxides of nitrogen.

During the course of this research Smithells and Dent made the interesting observation, which will be referred to again in Chapter XXIV when the influence of moisture upon combustion is discussed, that the outer cone of the flame of well-dried cyanogen could be extinguished by bringing a bottle of dry air over it, provided that the two cones were more than a certain distance apart; at lesser distances apart, however, no such extinction could be effected.

Smithells' researches also shed new light upon the structure of ordinary luminous hydrocarbon flames, and more particularly upon the genesis of what he called the 'blue calyx' at the base of them, as well as upon the correlation of structure and chemical interactions generally throughout them.

In a paper entitled "The Spectra of Carbon Compounds" * he dealt (*inter alia*) with the spectrum—first mapped in detail by Swan in 1857, and hence often called the 'Swan Spectrum'—seen in all ordinary hydrocarbon flames, and he shewed strong reasons for the supposition that it is due to the formation of carbonic oxide in the flame, although, in view of recent developments in spectroscopy, this conclusion may have to be modified. In this connection he shewed that "if the hydrocarbon is burnt without previous admixture with air, the region which gives the spectrum is visible as a bright blue sheath investing the lower part of the flame like the calyx of a flower. This part of a flame has often been confused with what is otherwise distinguished from it as 'the mantle'; but this mantle is really distinct from it. The blue calyx thins off gradually from below upwards, and is no longer visible when the bright yellow glow of the flame is intense, whilst the mantle surrounds the calyx and invests the whole ‘flame.’ He also shewed that the Swan Spectrum is given by the inner cone of a Bunsen flame, and inferred “that the blue calyx of a luminous flame corresponded chemically with the inner cone of a Bunsen flame.”

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* *Phil. Mag.* (1901), pp. 474–503.

Finally, it should be pointed out again that Smithells’ researches, read in conjunction with those of H. B. Dixon during the same period, afforded important evidence of the essential similarity between the chemical aspects of combustion in ordinary flames and in the ‘explosion wave.’

Temperatures of Flames

The term ‘flame temperature’ is sometimes used very carelessly in scientific literature, and indeed it is difficult to assign a precise meaning to it. For, as Smithells has truly observed, “most flames are composed of thin films, and their external surface includes a large quantity of unburnt gas,” so that whilst “we speak of the temperature of such a flame as measuring the average thermal stage of the burning film and the included gas” it is usual to mean “the temperature which would be indicated by a thermometric instrument wholly immersed in the region of combustion.” *

Another point which needs to be mentioned here is the importance, when using the term ‘flame temperature,’ of clearly indicating what part of the flame is meant or referred to, because flames usually have considerable volumes, and different regions in them have widely different temperatures.

The temperature of a stationary flame produced by burning gases issuing from a jet into air or other supporting atmosphere must presumably be governed or influenced by three factors, namely: (i) the ratio of the thermal value of the reaction to the corresponding total heat capacity of the products at constant pressure, (ii) the amount of energy directly radiated from the flame, and (iii) the rapidity with which the remaining energy is transformed into sensible heat of the products. Howbeit, any calculation of it made on such lines is at best difficult and uncertain, because assumptions necessarily have to be made which can only be approximate. For, not only is our knowledge of the specific heats of steam, carbon dioxide and nitrogen at high temperatures imperfect, but also the measurements which have so far been made of the energy directly radiated from flames can hardly be considered very precise. Also, as yet we hardly know sufficient about the relative times taken with various gas-air mixtures to effect the transference to the products of the energy developed by the combustion (less that directly radiated away) to warrant our assuming that in ordinary flames, such as we are now considering, the process is rigidly adiabatic, although probably it is nearly so.

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* Article on “Flame,” *Thorpe’s Dictionary of Applied Chemistry*, 1922 ed. vol. iii. p. 210.

Nevertheless, whilst fully recognising the foregoing limitations, it is sometimes instructive to make calculations of a *relative* character, for purposes of comparison with the maximum temperatures of flame which have actually been observed by the best workers, using pyrometric methods, during recent years.

In making such calculations it seems best (i) to take the *net* heat of combustion of the gas as representing the true index of the heat liberated for flame temperature purposes, (ii) to adopt mean values for heat capacities of carbon dioxide, steam, and nitrogen between 0° C. and 2000° C. (100° and 2000° C. in the case of steam) extrapolated from Holborn and Hennings' well-known curves, and (iii) to make allowance for radiation on the basis of H. L. Callendar's experiments and those of R. von Helmholtz, which will be referred to later. Calculating on such lines, and assuming complete combustion of the gas in the theoretical amount of air, we should arrive at the mean flame temperatures somewhat as follows :

	°C.
Hydrogen	1920°
Carbonic oxide	1700°
Methane	1670°
Ethylene	1900°
Acetylene	2320°

In actually measuring the mean temperature at any particular region in a flame, it is highly important that the instrument employed should have the smallest possible dimensions consistent with convenience and accuracy, because it must be immersed in the region whose temperature is being measured. For this reason most modern investigators have employed thermo-couples (usually platinum-platinum rhodium couples) of wires as thin as can be used without melting them, applying ' corrections ' for loss of heat by conduction and radiation. Such determinations, however, must be subject to various ' errors ' which it is difficult to allow for ; nevertheless, there are no better means available.

One way of applying such ' corrections,' which has been used for ' conduction ' losses when a thermojunction is immersed in a flame, consists in employing a series of thermojunctions of wires of diminishing diameter ; and, after plotting on a curve temperatures against diameters, to exterpolate so as to find the temperature at an infinitely small diameter. A German investigator, Waggener, adopted such a plan in 1896. Another investigator, Berkebusch, also compensated for loss by ' radiation ' from the thermocouple immersed in a flame by passing through the couple a known electric current which, by previous trial, had been found just sufficient for this purpose.*

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* An excellent general account of the employment of thermo-junctions for measuring flame temperatures was given by Prof. A. Smithells in a lecture before the Institute of Gas Engineers in 1905 (*Trans. Inst. of Gas Eng.*, 1905, p. 117).

The highest temperatures observed by some modern investigators for a Bunsen coal-gas flame, using the thermojunction method, have been as follows :

Highest Temperature observed in a Bunsen Coal-gas Flame

		°C.
1896	Waggener	1770°
1899	Berkebusch	1830°
1902	White and Travers	1780°

In 1904 Féry, who used an optical method based upon the reversal of the *D* line of sodium vapour in a flame, when viewed against an electric filament of known and alterable temperature, published the following results :

Highest Flame Temperatures observed by Féry

	°C.
Bunsen coal-gas flame (fully aërated)	1871°
Acetylene flame in air	2548°
Hydrogen flame in air	1900°
Oxy-coal gas blowpipe flame	2200°
Oxy-hydrogen blowpipe flame	2420°

CHAPTER XVIII

RADIATION FROM FLAMES

Introduction

In general the molecules of a gas can possess three types of energy, namely: (i) *translational* or kinetic (k), due to external movement of the molecules as a whole, causing temperature and pressure; (ii) *rotational* (r), or movements *within* each molecule caused by collision with others; and (iii) *vibrational* (v) which, though affected by collisions, is primarily connected with the absorption and emission of radiation. Hence, in general, the total energy of a molecule (Σ) at a given instant may be expressed as the sum of its three types, *i.e.*

$$\Sigma = k + r + v.$$

In other words, the energy of a gas is due in part to translational motion of its molecules as a whole, and in part to motions of some sort internal to its molecules. The translational part causes temperature and pressure; the other part produces no external physical effect except radiation, although, at ordinary temperatures, when energy is put into a gas, the rise in temperature, or pressure, corresponds to only a portion of the whole. It is thus necessary to distinguish between the '*kinetic energy*' of the gas and its '*internal energy*.' And, in regard to the latter, it is customary to distinguish between that which originates in vibrations within the molecule—called the '*vibrational energy*' and manifested as radiation—and that which is due to slower movements—the *rotational energy*—which produces no external physical effects.*

It should also be understood that whenever a gas is in a steady state of thermal equilibrium with its environment its three types of energy bear definite ratios to one another, dependent upon temperature and pressure. Also, that, if there be any sudden change in its temperature or pressure, a certain time must elapse before equilibrium with the new environment is re-established.

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* A lucid account of modern theories as to the nature and origin of the three types of energy possessed by gases is given in Lewis' *System of Physical Chemistry*, vol. iii., "Quantum Theory" (Longmans, Green & Co. 1918), to which readers are referred.

When an explosive gaseous medium in equilibrium with its environment is ignited, a very sudden and violent change occurs, whereby new molecules are born at a high temperature in an intensely vibrational condition. It is probable that, in the first instance and momentarily, the energy of the newly-born molecules is mainly internal ; and that a certain time interval must elapse, during which a rapid process of adjustment between the internal and kinetic energies occurs, before the medium re-attains a steady state of equilibrium with its environment. Indeed, it may be said that, in general, if T be the maximum mean temperature of the medium on explosion, in all probability its ‘ energy distribution state ’ is momentarily different from that which would result had the products of combustion merely been heated up to that temperature. In other words, it is generally agreed that the chemical changes occurring in flames and explosions do generate molecular systems whose energy is, in the first instance, largely vibrational ; and that a definite, though it may be small, time interval must elapse before the energy becomes mainly kinetic, and the system re-attains equilibrium with the environment.

It should, therefore, be understood that part of the total energy developed by the combustion of a gas in flames is directly radiated away, and consequently does not appear as sensible heat in the products, or contribute to the flame temperature.

The radiations so emitted may comprise widely different wave lengths, from low-frequency radiations in the infra-red up to high-frequency radiations in the ultra-violet ; and each flame has its own characteristic spectrum, according to the chemical changes occurring in it. And the study of such spectra, whether in the infra-red, or the visible, or the ultra-violet regions, powerfully assists our interpretation of flame reactions.

Without entering into a detailed discussion of modern theories of radiation, which is outside the scope of this book, it may be said that, according to Planck's conception, exchange of energy between matter and ether, instead of being continuous, as was formerly supposed, takes place in multiples of a small energy unit, called the *quantum*, which is a function of the vibration frequency concerned. From such standpoint the emission of radiant-energy from a burning system is essentially discontinuous and ‘ atomic.’ The vibrating entities producing ‘ visible ’ and ‘ ultra-violet ’ radiation are probably of much smaller dimensions than the atoms of the emitting bodies, and are usually thought to be the *electrons*. On the other hand, it is generally agreed that radiations emitted by vibrating *atoms* are confined to the infra-red region.

In this connection it is important to remember that what is termed ‘ the quantum ' is *not* a fixed quantity of energy but a function of the vibration frequency ; for, according to Planck, its magnitude,

$$\epsilon = hv,$$

where v = the frequency, and h a natural constant,

$$= 6 \cdot 5 \times 10^{-27} \text{ erg seconds.}$$

If now a system consisting of molecules, atoms and electrons (*i.e.* if different ' resonators ') be considered, it will be evident that the ' quantum ' corresponding to a high frequency in the ultra-violet would be very large compared with that corresponding to a low frequency in the infra-red region of the spectrum, and therefore that, *ipso facto*, the probability of its being emitted is relatively small. On such lines attempts have been made to account for the well-known fact that, in ordinary flame-combustion, and like changes, the *proportionate* energy-emission as radiation rapidly falls off in the visible and ultra-violet regions, as compared with what it is in the infra-red. Indeed, it has been estimated that upwards of 90 per cent. of the total radiation from ordinary flames is in the infra-red region.

On the other hand, if v be very small, as it is in the case of very long wave lengths, the magnitude of the ' quantum ' (ϵ) is also correspondingly small, a circumstance which implies a rapid curtailment of the proportionate energy emission of low frequency radiations.

Bearing in mind that, with a black body at 1370° C., the region of greatest emission intensity is 2μ in the infra-red, whilst, with one at 6000° C. it would be about $0 \cdot 5\mu$ in the visible region, it may be expected that the maximum emission intensity for ordinary flames, whose highest temperatures are usually somewhere about 2000° C. will probably be in the infra-red ; although, from a chemical point of view, the visible and ultra-violet rays, which probably originate in electronic displacements, are in some respects the more important. In considering the radiation from ordinary flames we may regard as negligible anything outside the limits of 8μ or thereabouts in the infra-red, and $0 \cdot 2\mu$ in the ultra-violet.

The British Association Committee's Report, 1910

The subject of radiation from flames was dealt with at some length in the " Third Report of the Committee appointed by the British Association in the year 1908 for the Investigation of Gaseous Explosions, with special reference to Temperature," and we cannot do better than consider here some of the more important points raised in it.*

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* *British Association Reports* (Sheffield), 1910, p. 469. The authors, one of whom served on the Committee, desire hereby to acknowledge their indebtedness to this Report for much information on the subject.

Experiments by R. von Helmholtz and W. H. Julius

The earliest attempts to measure accurately the total radiation emitted by flames were made by R. von Helmholtz in the year 1890. Unfortunately he worked only with small flames ; he found a non-luminous 'solid' coal-gas flame 60 mm. high and 6 mm. in diameter to radiate away about 5 per cent., a carbon monoxide flame about 8 per cent., and a hydrogen flame about 3 per cent., of the total energy developed by the combustion. Later on we shall see how, in 1910, H. L. Callendar, working with larger flames, found that a non-luminous coal-gas flame 30 mm. in diameter radiated away as much as 15 per cent. of the energy represented by the *net* heat of combustion.

In 1890, also, W. H. Julius of Berlin made a spectroscopic analysis of the infra-red radiation from different kinds of flames, which shewed it to be due to incipiently formed (or forming) CO_2 and H_2O molecules. Using a rock-salt prism he found that in all flames producing both CO_2 and H_2O most of the radiation was concentrated in two principal bands, of wave lengths 4·4μ and 2·8μ respectively. When pure hydrogen was burnt the 4·4μ band disappeared, but the other remained ; whereas, when carbonic oxide was burned the 2·8μ band disappeared, but the 4·4μ band remained. Hence, it seemed that the 4·4μ band is due to incipiently formed (or forming) CO_2 molecules, and the 2·8μ band to incipiently formed (or forming) H_2O molecules, a view which is generally accepted.

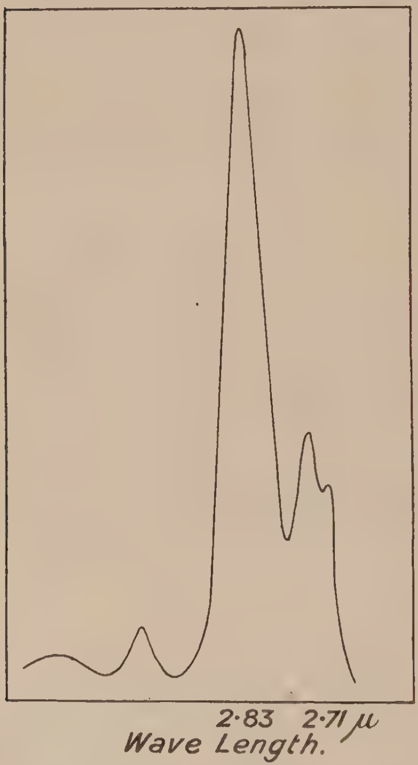

FIG. 87.—DISTRIBUTION OF ENERGY IN THE INFRA-RED OF THE RADIATION FROM AN ELECTROLYTIC GAS FLAME. (Paschen.)

Some Infra-Red Emission Spectra from Flames

As illustrating the foregoing paragraphs we perhaps cannot do better than direct attention to the infra-red spectra of a hydrogen detonating gas flame (Fig. 87) and of a coal-gas Bunsen flame (Fig. 88) taken from papers published by Paschen in the years 1893–4. He also made a systematic investigation

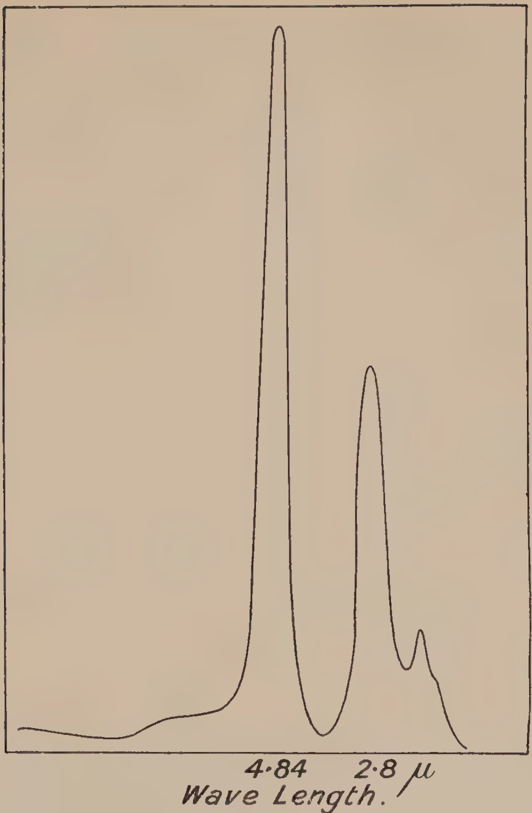

FIG. 88.—DISTRIBUTION OF ENERGY IN THE INFRA-RED OF THE RADIATION FROM A BUNSEN FLAME. (Paschen.)

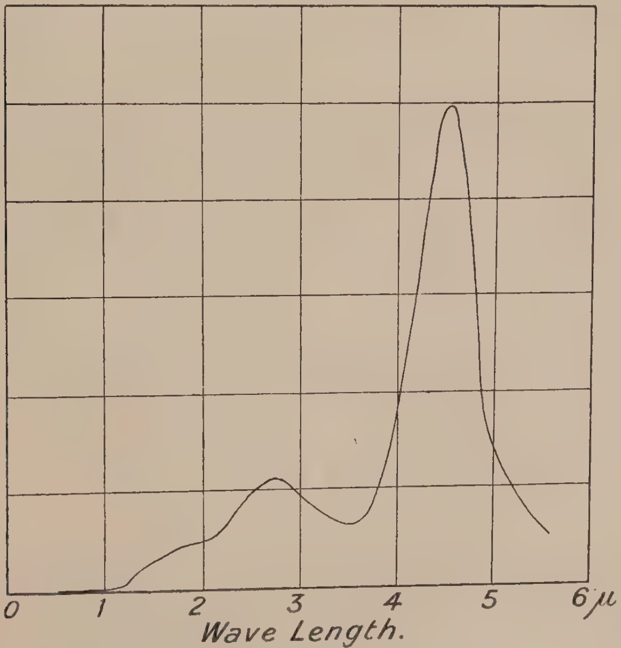

FIG. 89.—DISTRIBUTION OF ENERGY IN THE INFRA-RED OF THE RADIATION FROM THE ISOLATED INNER CONE OF A BUNSEN FLAME. (Reproduced by the kindness of Radiation, Ltd.)

of the emission bands of CO_2 and H_2O, finding that the characteristic CO_2-band shifts towards the long wave-lengths with rise in temperature. Thus at 600° C. its maximum was at 4·3μ, at 1000° C. at 4·388μ, and at the temperature of the Bunsen flame at 4·40μ. In this connection it may be noted that in 1905 W. W. Coblentz made experiments which led him to conclude that carbonic oxide gives a strong emission band whose maximum is at 4·75μ. It must be remembered, however, that at the high maximum temperatures prevailing in flames CO_2 is partly dissociated, and what we have to do with is probably a reversible $CO_2 \rightleftharpoons CO + O$ system.

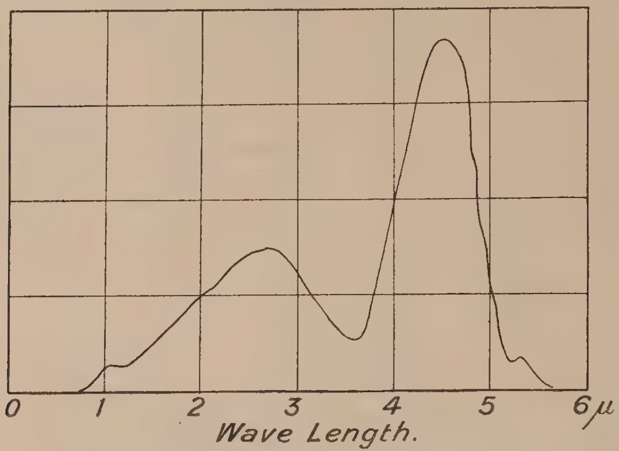

FIG. 90.—DISTRIBUTION OF ENERGY IN THE INFRA-RED OF THE RADIATION FROM THE ISOLATED OUTER CONE OF A BUNSEN FLAME.
(Reproduced by the kindness of Radiation, Ltd.)

We are indebted to the kindness of Radiation Ltd. of London for permission to reproduce in this connection two interesting curves (Figs. 89 and 90), embodying the results of experiments recently made in their Research Laboratories, under the direction of Dr. Harold Hartley, shewing the distribution of energy in the infra-red vibrations, (*a*) from the *inner* cone of an aërated coal-gas flame in a Smithells' separator, the cone being viewed through a quartz window, and (*b*) from the *outer* cone of the same flame. Although the maximum intensities of radiation obtained in the two cases are not directly comparable, the relationship between that of the steam at 2·72μ and that of the CO_2 band at 4·45μ is ; and it is interesting to observe that the *relative* amount of radiation due to the steam band is greatest in the inner cone.

R. von Helmholtz's Experiments (Continued)

In the course of his researches R. von Helmholtz measured by means of a bolometer the relative amounts of radiation, per litre of gas burnt, emitted by flames of given size burning various gases, the air supply in each case being adjusted so that the flame was just non-luminous, with the following results :

Gas Burnt.	Relative Radiation per Litre.
Hydrogen	74
Carbonic oxide	177
Methane	327
Ethylene	570

The important things to observe about these results are (i) that a carbonic oxide flame has an infra-red radiating power, for a given volume of gas burnt, nearly 2·4 times that of a hydrogen flame of similar dimensions, and (ii) that the relative infra-red radiation power of a hydrocarbon flame, such as that of methane or ethylene, is apparently determined by the number of steam and carbon dioxide molecules produced from a given volume of gas burnt. Thus the observed value of 327 per litre for methane burnt was, within experimental error, equal to the 177 observed for carbonic oxide *plus* twice the 74 observed from hydrogen

$$(177+2\times 74=325),$$

a result which agrees well with the supposition that in such cases the radiation is due to incipiently formed (or forming) carbon dioxide and steam molecules.

It should here be noted that, whilst R. von Helmholtz took the view that the infra-red radiation from such flames is mainly due to molecules which have just been formed, and are, therefore, in a highly vibratory condition—or, in other words, that, like the visible and ultra-violet radiation, such radiation is due to *chemical* rather than *thermal* cause—Paschen and others have maintained that it is purely thermal. Probably most chemists prefer the former view, whilst recognising that the matter is by no means '*une chose jugée.*'

Without dogmatising on the subject, the authors would attribute the radiation from non-luminous flames to the formation *at the instant of combustion* of intensely vibratory hydrogen-oxygen, carbonic-oxide-oxygen, methane-oxygen, etc., 'complexes' which eventually give rise to steam and carbon dioxide molecules. Thus, for example, in the case of a hydrogen flame, hydrogen and oxygen molecules meeting in collision may be considered as forming, in the first instance, and for an indefinitely short period, not steam, but an intensely vibrational system of hydrogen and oxygen. There would be violent disturbances and rearrangements of electronic orbits, extending to the expulsions of electrons previously bound. Such a system, during its transient existence, would emit a considerable amount of radiant energy, which would not, therefore, appear as sensible heat in the products. Afterwards would come the formation of steam, at first in a highly vibratory condition, until finally the system would settle down to a state of ' equilibrium ' with its environment, so that its relative translational (kinetic) and internal (rotational or vibrational) energies would correspond with the temperature of the environment, after which the system would gradually lose translatory energy (temperature) by ordinary cooling processes, automatically adjusting its ' energy distribution ' *pari-passu* with the falling temperature.

H. L. Callendar's Experiments with Stationary Flames

In connection with the work of the British Association Committee on Gaseous Explosions (*loc. cit.*) H. L. Callendar carried out some notable quantitative measurements of the energy radiated away from coal-gas flames of various sizes burning under different conditions. An Angström pyrheliometer, whose constant was checked by means of a radio-calorimeter and also an absolute measuring bolometer, was employed, and the measurements were made in calories per square cm. per minute. The results indicated that, with gas and air adjusted in substantially the proportions required for complete combustion, the total energy radiated away depended largely on the size of the flame, as well as on its temperature; for it varied from 10 to 15 per cent. of the total energy generated by the combustion as the diameter of the burner was increased from 1 to 4 inches.

Callendar also made measurements with a Méker burner, consuming coal-gas at the rate of 0·185 cubic foot per minute. With full air supply, the gas and air being in the proportions required for complete combustion, a ' solid ' homogeneous conical pointed flame, with no indication of an inner cone, was obtained. On gradually reducing the air-supply, however, minute inner cones made their appearance over the grid of the burner, and finally coalesced into a single steady brilliant inner cone, which increased in size. The percentage of the total *net* heat of combustion which was radiated away increased from 10·5, with full air-supply, up to 16·0 as a maximum, with a large and bright inner cone. Beyond this point the flame began to flicker, and the radiation soon dropped to 14 per cent., rising again to 17 per cent. as the air-supply was further reduced, and the flame became luminous. The results are epitomised as follows :

Table XLIX.—Radiation from Méker Burner (Callendar)

Total Radiation of Méker Burner, per cent. of Net Heat of Combustion.

Ratio air/gas by volume - - -	5	4	3	2·5	1·5	1	0
Percentage of net heat of combustion radiated	10·5	12·3	14·0	15·9	14·1	14·6	17·0

Callendar found, however, that what might be termed the ‘intrinsic radiation’ of the flame—which, in view of its transparency to its own radiation, should be measured per unit of solid angle subtended by the recording instrument (*e.g.* a total radiation pyrometer of any kind in which an image of the flame is formed on a radiometer or bolometer)—did not vary materially as the air supply was reduced from that required for complete combustion until the inner cone became so large that the flame could no longer be regarded as sensibly homogeneous. This, he said, shewed “that the increase of total radiation simultaneously observed was due chiefly to increase in the size of the flame, and that the increase of thickness of the flame was compensated either by fall in temperature or by increase in absorptive power.”

Special measurements, made to determine how the intrinsic radiation R varied with the thickness x of the flame in the line of sight and to measure the coefficient of absorption, gave results in agreement with the expression:

$$R=473(1-e^{0\cdot 054x}),$$

and shewed how surprisingly transparent such flames are to their own radiation.

With regard to the influence of size of flames upon their radiating powers the British Association Committee reported as follows: “The size of the flame affects the matter in two ways. In the first place, a large flame radiates more per unit of area than a small one, because a flame is to a great extent transparent even to its own radiation, so that the radiation is received not only from molecules at the surface of the flame, but also from those at a depth within it. . . . The second point is that the cooling of the gas is slower in a large flame than in a small one. The radiation originates in the vibration of the CO_2 and steam molecules, and the life of one of these molecules as a radiating body extends from the moment of its formation to the time when its vibrational energy has been destroyed by radiation and by collisions with colder molecules, such as those of the air surrounding the flame. The smaller the flame the more rapid will be the extinction of the vibrations, and the less, therefore, the total amount of radiation per molecule.”

B. Hopkinson's Experiments on Coal-gas Air Explosions

In 1910 the late B. Hopkinson, assisted by W. T. David, measured the total radiation emitted during a coal gas-air explosion in a closed cylindrical vessel (30 cm. × 30 cm.), and throughout the subsequent cooling period.* The explosive mixture employed always consisted of 15 parts of coal-gas (gross calorific value 6 K.C.US. per litre at N.T.P.) with 85 of air, such being very nearly the mixture of maximum strength consistent with complete combustion. The mixture was always fired at atmospheric temperature and pressure; the products of combustion contained about 8·5 per cent. of CO_2, 20 per cent. of H_2O, the remainder being nitrogen with a small amount of excess oxygen. Two comparative sets of experiments were made, namely: (i) with the walls of the vessel highly polished, and (ii) in which they were painted with a 0·02 mm. layer of a dead-black lamp-black mixed with a little shellac. The explosion vessel was fitted with a fluorite window, outside of which was fixed a resistance-bolometer, made of a blackened platinum strip, for measuring the radiation emitted.

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* *Proc. Roy. Soc.* A. 84 (1910), pp. 155 to 172.

The results shewed that the *total* energy radiated during and after the explosions amounted to over 22 per cent. of that represented by the *gross* calorific value of the gas; howbeit, during the explosion—*i.e.* up to the attainment of maximum pressure—only about one-seventh of the total radiation had been emitted. It was stated that the percentages referred to were calculated " on the assumption that the radiant heat is absorbed by every part of the blackened walls at the same rate as by the bolometer, no allowance being made for absorption in the fluorite or reflection from the bolometer," and it was considered that about 10 per cent. should be added to get the true amount of radiation. It was also shewn by W. T. David that in all probability the radiation emitted in such an explosion consists almost entirely of the same two bands ($4{\cdot}4\mu$ and $2{\cdot}8\mu$ respectively) as are emitted by an ordinary Bunsen flame.

Influence of Temperature and Pressure

Very little is definitely known as yet concerning the influence of temperature and pressure upon the radiation emitted during gaseous explosions, and the subject needs so much further experimental investigation that the wise will be wary of committing themselves to any settled views on the subject. As regards pressure, the British Association Committee were content merely to say that " within moderate limits of pressure the radiating and absorbing powers of a flame per unit thickness at a given temperature and composition should vary directly as the pressure or density." And in regard to temperature they remarked that, although Nernst had considered the radiation to vary as the fourth power of the temperature, " his conclusion was most severely criticised by Lummer, Pringsheim and Schaefer, who explained that the radiation was quite different from that of the black body, and that the quality of the radiation was little, if at all, affected by pressure up to four atmospheres." Also, they pointed out that, according to Planck's formula for a single wave length, the rate of variation " is much slower than the fourth-power law, and tends in the limit to be directly proportional to the absolute temperature at high temperatures, and therefore

" the actual rate of variation should lie between these limits, but nearer to Planck, *unless carbon begins to separate in rich mixtures at high temperatures.*"

It may be mentioned that during the course of the researches upon gaseous combustion at high pressures, which the authors have carried out in conjunction with Dr. D. M. Newitt at the Imperial College, London, some light has been thrown on these aspects of the problem, and that we propose discussing them further in our proposed supplementary volume on high-pressure explosion work.

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SECTION III

CHAPTERS XIX TO XXIII

GASEOUS EXPLOSIONS IN CLOSED VESSELS

CHAPTER XIX

EARLY EXPERIMENTS ON GASEOUS EXPLOSIONS IN CLOSED VESSELS

Up to the end of last century the most important work upon gaseous explosions in closed vessels had been the classical researches of the French chemists Berthelot and Vieille and Mallard and Le Chatelier, who were investigating the purely scientific aspects of the problem, and of Dugald Clerk in this country, who was then working on the development of the gas engine. Their work laid the foundations on which nearly all subsequent advances in our knowledge of the subject have been based.

It may be recalled that the pressures developed in gaseous explosions were first measured by Hirn * in 1861, and later by Bunsen in 1867. By means of a Bourdon manometer Hirn recorded a pressure of 3·25 atmospheres in an explosion of a mixture of 10 per cent. hydrogen in air, compared with 5·8 atmospheres on the assumption of constant specific heats and adiabatic conditions; he also measured pressures of 7 and 5 atmospheres for explosions of mixtures of 20 per cent. hydrogen in air and 10 per cent. coal-gas in air, respectively, these values also being much lower than those similarly calculated. He attributed the low pressures attained in such explosions to the fact that the metal sides of the explosion vessel were at so low a temperature compared with that of the explosion itself that the heat was rapidly conducted away.

An outline of Bunsen's experiments † has already been given in Chapter VI. He eliminated, as far as he was able, the effect of cooling loss by firing explosive mixtures by means of a powerful electric spark passed from end to end of his narrow explosion tube, believing that the whole of the gas would be inflamed in less than $\frac{1}{4000}$th of a second. His results may be said to have established the fact, confirmed by all subsequent workers, that the pressure developed in a gaseous explosion is considerably less than that which would result if (*a*) there were no heat loss, (*b*) combustion were complete, and (*c*) specific heats were independent of temperature.

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* *Zur Theorie der Lenoirschen Polytechnische Central–Blatt Gasmachinen*, Leipsic, 1861; see also Clerk, *The Gas, Petrol and Oil Engine*, vol. i. p. 134.

† *Pogg. Ann.* 131 (1867), 161, and *Phil. Mag.* 34 (1867), 489, or *Gasometriche Methoden*, 1877.

Bunsen's apparatus afforded no means of measuring the relative rates of attainment of maximum pressure in explosions of gaseous mixtures. For this purpose a self-registering manometer was necessary, and different types of such instruments have been employed in most subsequent researches.

Berthelot and Vieille's Experiments

After some preliminary investigations by Vieille in 1882–1883,* whereby the practicability of his apparatus was established, he was joined by Berthelot,† the summarised results of their researches appearing in 1885.

Berthelot had already shewn in 1877 that Bunsen's calculations of explosion temperatures were inadmissible,‡ for in 1871 it had been demonstrated by Regnault that the specific heat of carbon dioxide increases considerably between 0° and 200° C. Moreover, he supposed that the same would apply to other gases, the more so at very high temperatures. Accordingly he considered that if combustion were complete and the heat of reaction known, there would be no difficulty in calculating the mean specific heats of the exploded gases from the maximum temperature deduced from the known pressure development in any particular case. It was still necessary, however, to consider the question of dissociation, which might have an influence on the explosion temperatures so calculated. Thus he proposed the calculation of two temperatures between which the correct value would lie, assuming on the one hand complete chemical contraction in volume on combustion and on the other no contraction. Thus:

$$T_2=\frac{P_2}{P_1}\times T_1\times\frac{1}{m}, \text{ or } T_2=\frac{P_2}{P_1}\times T_1,$$

where m = the ratio of the volume of the gaseous products to that of the initial gases.

With the object of testing these considerations, and of estimating the probable specific heats of the principal gases at high temperatures, Berthelot and Vieille thoroughly investigated the explosions of a very wide range of gaseous mixtures when fired at atmospheric temperature and pressure in their bombs.

They employed an indicator of the type designed by Sebert and Ricq for work with solid explosives. It consisted essentially of a closely fitting piston of about 1·5 cm. diameter, to which was attached a pen point so arranged as to trace a trajectory on a piece of blackened paper fastened round a revolving cylinder, whose peripheral speed was about 10 to 15 metres per second. An electrically operated tuning-fork traced its vibrations on the same paper, so that the displacement-time curve could easily be interpreted. From this curve the maximum acceleration imparted to the piston was determined, and with a knowledge of its mass and cross-section the pressure exerted by the explosion could readily be estimated.

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* *Comptes rendus*, 95 (1882), p. 1280; 96 (1883), pp. 116, 1218, and 1360.

† *Comptes rendus*, 96 (1883), p. 1186; 98 (1884), pp. 545, 601, 646, 705; and *Ann. Chim. Phys.* 6 ser. iv. (1885), p. 13.

‡ *Ann. Chim. Phys.* 5 ser. xii. (1877), p. 302.

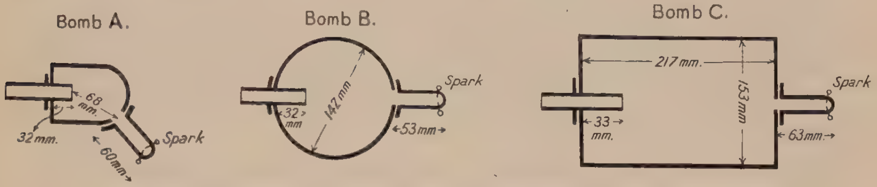

Fig. 91.—Types of Bombs used by Berthelot and Vieille.

In order to gain some information concerning the possible cooling influence of the walls upon the pressures recorded, three bombs of different capacities—namely, *A*, of 300 c.c., *B*, of 1500 c.c., and *C*, of 4000 c.c.—were employed. These are illustrated in outline in Fig. 91, and the data relating thereto are summarised in the following table:

Table L.—Details of Bombs Employed by Berthelot and Vieille

Bomb.	*A*.	*B*.	*C*.
Capacity in cm³.	300	1500	4000
Surface in cm².	216	648	1220
Surface per unit volume	0·72	0·43	0·33
Diameter in cm.	6·0	14·2	15·3
Length of firing piece in cm.	6·0	5·3	6·3
Travel of flame before reaching the piston in cm.	12·8	16·3	24·8

Bomb *A* was cylindrical in form, having one end flat and the other hemispherical. The tube carrying the indicator piston was led into the flat end and protruded into the interior of the bomb for a distance of 32 mm. A tube 60 mm. long and 5 mm. in diameter was fitted at the junction of the cylindrical and hemispherical parts of the bomb, the mixtures being fired at the end of this tube by means of an electric spark. The distance travelled from the point of inflammation to the piston head was in all 128 mm., of which 68 mm. were in the bomb itself.

Bomb *B* was spherical, with an internal diameter of 142 mm. The firing tube was 53 mm. long and 5 mm. in diameter, and was situated exactly opposite the piston-carrying tube, which protruded a distance of 32 mm. into the bomb. The distance thus travelled by the flame from the point of inflammation to the piston head was therefore:

$$142 + 53 - 32 = 163 \text{ mm.}$$

The large bomb *C* was a cylinder of length 217 mm. with flat ends, one carrying the firing tube (in this case 63 mm. × 5 mm.), the other the piston-carrying tube, which also protruded a distance of 32 mm. into the bomb. In this case the distance travelled by the flame was:

$$217 + 63 - 32 = 248 \text{ mm.}$$

Berthelot and Vieille first of all set out to determine the differences between the maximum pressures developed in explosions of similar gaseous mixtures in the smallest and largest of the three bombs. As might be expected, they found greater pressures developed in the largest bomb where the surface/volume ratio was least. They concluded that for all practical purposes their largest (4 litre) bomb could be considered as of infinite size (*i.e.* having no cooling effect), and that pressures determined experimentally in the smallest bomb (300 c.c. capacity), could be corrected for cooling loss by multiplying them by a factor (usually about $1\frac{1}{9}$). Thus they said: "*les plus grands fournissent les plus fortes pressions, comme on pouvait s'y attendre, à cause de l'influence refroidissante des parois, influence que la petitesse des récipients tend à exagérer. Nous avons déterminé cette influence en opérant sur les mêmes mélanges dans les deux capacités extrêmes, et nous en avons déduit la correction (voisine de* $\frac{1}{9}$*) qu'il convient d'appliquer aux pressions mesurées dans le petit recipient, toutes les fois que ce dernier a été seul employé,*" and they gave the following figures which had not previously been corrected in any way:

TABLE LI.—SHEWING PRESSURES DEVELOPED IN BOMBS OF VARYING CAPACITY (BERTHELOT AND VIEILLE)

Gaseous Mixture.	Pressures Developed (Atmospheres).		Bomb *A*./Bomb *C*.
	Bomb *A*.	Bomb *C*.	
$2H_2 + O_2$	7·41	9·69	0·76
$2H_2 + O_2 + 2N_2$	7·60	8·63	0·88
$2H_2 + O_2 + 4N_2$	7·34	7·55	0·95
$2H_2 + O_2 + 6N_2$	6·12	6·64	0·92
$2CO + O_2$	9·29	9·93	0·93
$C_2H_4 + 3O_2$	14·18	15·73	0·90
$CH_4 + 2O_2$	13·94	14·81	0·94
	Bomb *A*.	Bomb *B*.	Bomb *A*/Bomb *B*.
$C_2N_2 + O_2 + 2N_2$	13·88	15·56	0·89
$C_2N_2 + O_2 + 1\frac{1}{2}N_2$	18·65	21·09	0·88

The value found in the case of the explosion of the $2H_2 + O_2$ mixture in Bomb *A* was rejected because they considered cooling to have been so rapid that "properly speaking a maximum pressure was not observed."

We will now give some of Berthelot and Vieille's results and the conclusions which they deduced therefrom. All the explosion pressure values, if determined in the smallest bomb, were corrected for cooling loss as described, and initial pressures were all reduced to 0° and 760 mm.

The figures given in Table LII shew the effect on the maximum pressure developed of additions of one or other of the reacting gases, as compared with nitrogen, when added as a diluent in the explosion of electrolytic gas.

TABLE LII.—INFLUENCE OF DILUENT GAS ADDED TO ELECTROLYTIC GAS ON THE RESULTANT EXPLOSION PRESSURE (BERTHELOT AND VIEILLE)

Corrected Pressures (Atmospheres).					
		$2H_2+O_2$	9·80		
$+2H_2$	8·82	$+2O_2$	8·69	$+2N_2$	8·75
$+4H_2$	8·02			$+4N_2$	7·94
$+6H_2$	7·06	$+6O_2$	6·78	$+6N_2$	6·89

It was noted that each of the three diluent gases lowered the maximum pressure to almost the same extent, from which the conclusion was drawn that the effects of dissociation are negligible in such explosions. For they said: "*On remarquera qu'elles ont les mêmes valeurs, que le gas inerte soit ou non l'un des composants du mélange: ce qui montre le peu d'influence exercée par cette condition sur la dissociation, ou plutôt la faiblesse même de la dissociation.*"

It was next found that successive dilutions of a $2CO+O_2$ mixture by nitrogen lowered the maximum explosion pressure more than had been observed in similar experiments with electrolytic gas, a result which was attributed to the comparative slowness of the carbonic oxide explosions. Thus they found:

Mixture.	Corrected Pressures (Atm.).
$2CO+O_2$	10·12
,, $+\frac{1}{2}N_2$	9·33
,, $+N_2$	8·77
,, $+2\frac{1}{2}N_2$	7·05

In the case of the explosion of cyanogen mixtures the following values were obtained:

TABLE LIII.—PRESSURES DEVELOPED ON EXPLODING VARIOUS CYANOGEN-OXYGEN-NITROGEN MIXTURES (BERTHELOT AND VIEILLE)

Partial Combustion.		Complete Combustion.	
	Corrected Pressures (Atmospheres).		Corrected Pressures (Atmospheres).
$C_2N_2+O_2$	25·11	$C_2N_2+2O_2$	20·96
,, $+\frac{1}{4}N_2$	20·67	,, $+N_2$	17·70
,, $+2N_2$	15·26	,, $+2N_2$	14·74
,, $+3\frac{3}{4}N_2$	11·78	,, $+4N_2$	12·33

Attention may be directed to the greater pressure development in the case of the partial combustion of cyanogen as compared with that in the case of its complete combustion, though in the light of H. B. Dixon's researches on the subject the explanation is not difficult.

As shewing the pressures developed when various combustible gases were exploded with oxides of nitrogen, the following figures are of interest :

	Corrected Pressures (Atmospheres).	
$H_2 + N_2O$	13·60	
$CO + N_2O$	11·41	
$C_2N_2 + 2N_2O$	26·02	Partial combustion.
$C_2N_2 + 2NO$	23·34	
$C_2N_2 + 4N_2O$	16·92	Complete combustion.
$C_2N_2 + 4NO$	22·66	

On exploding gaseous hydrocarbons with the theoretical amounts of oxygen required for their complete combustion it was found that in each of the following cases approximately the same pressure was developed :

		Corrected Pressures (Atmospheres).
Acetylene	$C_2H_2 + 2\frac{1}{2}O_2$	15·29
Ethylene	$C_2H_4 + 3O_2$	16·13
Ethane	$C_2H_6 + 3\frac{1}{2}O_2$	16·18
Methane	$CH_4 + 2O_2$	16·34

Berthelot and Vieille were also able to determine the relative rates of attainment of maximum pressure on exploding their various gaseous mixtures. This was accomplished by causing the recording pen, which was controlled electrically, to make a definite mark on the blackened paper the moment the igniting spark was passed. They found the speed of combustion to be very variable, and generally to correspond with conditions intermediate between detonation and ordinary combustion. As a rule the time required for the development of maximum pressure was longer the greater the capacity of the explosion vessel and the greater the distance between the point of inflammation and the indicator piston.

With carbonic oxide the time required was greater than with hydrogen, whilst in the cases of cyanogen and of hydrocarbons rich in hydrogen the time was practically the same as in the case of hydrogen itself. Moreover, they stated that the absolute rapidity of combustion was very difficult to estimate, but, assuming that the flame reached the piston at the moment when the maximum pressure was developed, the velocity of the combustion was about 100 metres per second for hydrogen, 8 metres per second for carbonic oxide and 70 metres per second for cyanogen. When nitrous oxide was employed the velocity of combustion of hydrogen was reduced to one half, and that of cyanogen to one-third.

As a comparison of the times taken from the moment of inflammation to that of the attainment of maximum pressure in two different bombs, the following figures were given :

TABLE LIV.—TIMES TAKEN FOR THE ATTAINMENT OF MAXIMUM PRESSURE IN EXPLOSIONS IN BOMBS OF VARYING CAPACITY (BERTHELOT AND VIEILLE)

Gaseous Mixture.	Time for Attainment of Maximum Pressure (sec.).	
	Bomb *A*.	Bomb *C*.
$2H_2 + O_2$	0·00104	0·00214
$2H_2 + O_2 + 2H_2$	0·00167	0·00422
$2H_2 + O_2 + 2N_2$	0·00267	0·00687
$2CO + O_2$	0·01286	0·01551
$C_2H_4 + 3O_2$	0·00286	0·00223
	Bomb *A*.	Bomb *B*.
$C_2N_2 + 2O_2$	0·00155	0·00450
$C_2N_2 + O_2 + 2N_2$	0·01035	0·01512

With regard to the combustion of cyanogen the following ‘ explosion times ’ were observed :

TABLE LV.—EXPLOSION TIMES OF VARIOUS CYANOGEN-OXYGEN-NITROGEN MIXTURES (BERTHELOT AND VIEILLE)

Time taken for Attainment of Maximum Pressure (sec.).
Bomb *A* (300 cc. capacity).

Partial Combustion.		Complete Combustion.	
$C_2N_2 + O_2$	0·00106	$C_2N_2 + 2O_2$	0·00155
$C_2N_2 + O_2 + 2N_2$	0·01035	$C_2N_2 + 2O_2 + 2N_2$	0·01540

from which they concluded that : “ *D'après ces nombres, il ne paraît pas que la combustion totale du cyanogène s'effectue en deux temps, en formant d'abord en totalité de l'oxyde de carbone qui brûlerait ensuite ; car la combustion totale est beaucoup plus rapide que la somme de ces deux effets séparés. Entre les deux modes, c'est la combustion incomplète qui est la plus rapide ; peut-être à cause de l'existence d'une dissociation partielle qui ralentit la combustion totale.*” In the light of more recent research this statement cannot be accepted entirely as it stands, for we now know that cyanogen *does* burn in two definite stages.

Finally, the times taken for the development of maximum pressures in explosions of mixtures of the following hydrocarbons with sufficient oxygen for complete combustion were as follows :

TABLE LVI.—EXPLOSION TIMES OF VARIOUS HYDROCARBON-OXYGEN MIXTURES (BERTHELOT AND VIEILLE)

	Bomb *A* (300 cc. capacity).	Sec.
Acetylene	$C_2H_2 + 2\frac{1}{2}O_2$	0·00194
Ethylene	$C_2H_4 + 3O_2$	0·00286
Ethane	$C_2H_6 + 3\frac{1}{2}O_2$	0·00083
Methane	$CH_4 + 2O_2$	0·00124
Methyl ether	$C_2H_6O + 3O_2$	0·00142
Ethyl ether	$C_4H_{10}O + 6O_2$	0·00289

Observing that the rate of combustion of the gases rich in hydrogen was very near to that of hydrogen itself it was concluded : "*Ce qui semble indiquer que l'hydrogen brûle avant le carbon, même dans les combustions totales*," an idea prevalent at that time.

Before leaving Berthelot and Vieille's work mention must be made of a series of experiments which were made in order to see whether or not the density of the initial gaseous mixture had any effect on the relative pressures produced; for, they said, if the pressures exerted by gaseous systems to which a given amount of heat has been communicated vary in the same ratio as their densities it will follow that the specific heat of the system is independent of its density, *i.e.* initial pressure, and will depend solely on its absolute temperature. In order to investigate this point two methods were adopted. The first consisted in exploding similar gaseous mixtures which previously had been heated to different temperatures, whilst the second and more accurate method consisted in exploding 'isomeric' mixtures, *i.e.* mixtures which originally contained the same elements in different states of combination, but are all brought into exactly the same conditions by the explosion.

In the case of the second method, if two 'isomeric' mixtures have densities Δ and Δ', then the relative molecular volumes V and V' may be expressed as $\frac{1}{\Delta}$ and $\frac{1}{\Delta'}$ respectively. If Q is the heat liberated and P the pressure developed, they found for the following two isomeric mixtures :

	V	Q (cal.).	P (atm.).
$2CO + 3H_2 + 2\frac{1}{2}O_2$	30	312·1	9·9
$C_2H_6O + 3O_2$	16	314·7	19·9

whence $$\frac{P'}{P} = 2{\cdot}0 \quad \text{and} \quad \frac{V}{V'} = 1{\cdot}9.$$

Similar results were obtained in many other experiments of this character, from which it was concluded that "*la chaleur spécifique des gaz est* *sensiblement indépendante de la densité, aussi bien vers les très hautes températures qu'au voisinage de* 0°."

Berthelot and Vieille's Specific Heat Values at High Temperatures

In order to determine the mean specific heats of the diatomic gases Berthelot and Vieille made use of a series of results obtained from the explosion of cyanogen mixtures. The data relating thereto are as follows:

TABLE LVII.—VALUES OF MEAN SPECIFIC HEATS OF NITROGEN AND CARBONIC OXIDE AT HIGH TEMPERATURES (BERTHELOT AND VIEILLE)

Mixture.	Maximum Pressure (Atms.).	Heat of Reaction (Cals.).	Temperature C°.	Apparent Specific Heat.	
				Total.	For N_2 and CO.
$C_2N_2 + O_2$ - -	25·11	126500	4394°	28·81	9·60
$C_2N_2 + O_2 + 1\frac{1}{2}N_2$	20·67	126500	4024°	31·46	8·39
$C_2N_2 + O_2 + 2N_2$	15·26	126500	3191°	39·67	7·93
$C_2N_2 + O_2 + N_2$ -	11·78	126500	2810°	45·05	6·67
$C_2N_2 + 2NO$ -	23·34	169800	4309°	39·39	9·85
$C_2N_2 + 2N_2O$ -	26·02	168400	3993°	42·17	8·43

From these figures they deduced the following equation for the relation between mean specific heat at constant volume and temperature (C°) in the case of all diatomic gases:

$$\bar{C}_v = 6{\cdot}7 + 0{\cdot}0016\,(T - 2800),$$

at the same time expressing the opinion that the values for oxygen would exceed slightly those for hydrogen.

Having found approximately such values for diatomic gases they next calculated those for steam from the experimental results of explosions of electrolytic gas with varying proportions of nitrogen, and deduced the following formula:

$$\bar{C}_v = 16{\cdot}2 + 0{\cdot}0019\,(T - 2000).$$

Similarly, from explosions of carbon monoxide and also of cyanogen, a similar formula for carbon dioxide was deduced, namely:

$$\bar{C}_v = 19{\cdot}1 + 0{\cdot}0015\,(T - 2000).$$

Although such equations do not give the values now usually accepted, they manifested the general order of the rise of specific heats of gases with temperature, and were in substantial agreement with results calculated independently by Mallard and Le Chatelier, working contemporaneously on the same problem, with whose researches we shall now deal.

Mallard and Le Chatelier's Researches

The researches of Mallard and Le Chatelier, which were carried out during the years 1880–1882, are of no less interest than those of Berthelot and Vieille. Working on behalf of the French 'Firedamp Commission' they aimed at deducing the combustion temperatures of various gaseous mixtures from measurements of the pressures developed on their explosion in a closed vessel, and at calculating therefrom the probable values for specific heats of gases at such high temperatures.* Their first apparatus, illustrated in Fig. 92, consisted essentially of a cylindrical glass explosion vessel (*A*), about 4 inches in height and 2 inches in diameter, provided with electrodes for central ignition. At the base connection was made to a Deprez manometer; this functioned by the movement of a piston (*C*) against a spring (*S*), the tension of which could be adjusted before each experiment by means of the tightening device *B*.

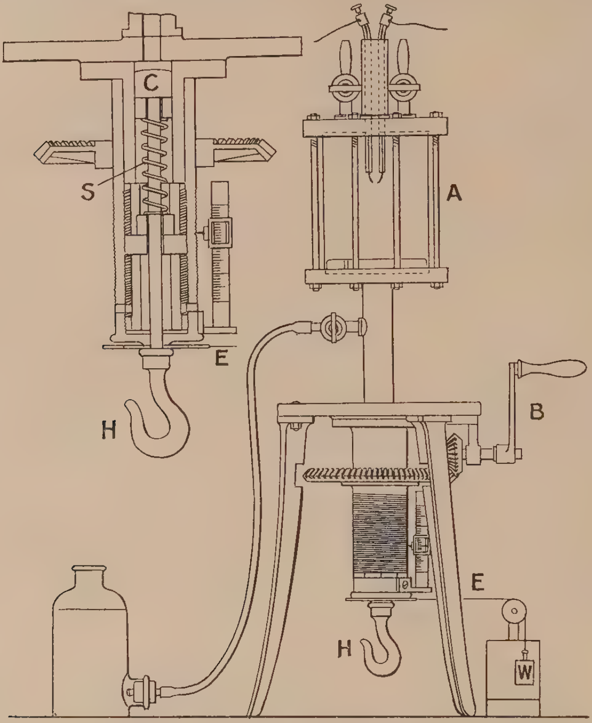

Fig. 92.—Mallard and Le Chatelier's First Explosion Apparatus with Deprez Manometer.

The load which was just sufficient to compress the spring was previously determined by actual test with definite weights which were loaded on the hook *H*. The duration of the explosion pressure was measured by the vertical distance which a weight (*W*) fell, its release being controlled by a cord (*E*), which was ordinarily firmly held by the action of the spring against the piston. It will thus be seen that the Deprez indicator formed a very delicate instrument for measuring pressure development of very short duration, for the most momentary pressure in excess of that represented by the tension of the controlling spring would be accompanied by a slight fall of the weight. Indeed, the great sensitiveness of the instrument cost Mallard and Le Chatelier much fruitless effort and finally led them to abandon its use entirely. They found that they were measuring local pressures of very short duration and of much greater intensity than that which could be developed by the explosive mixture as a whole, and which would represent the mean temperature developed in the explosion. In fact, they were measuring the pressure exerted not by the exploded gases as a whole but by high-compression waves set up in the explosive mixture, the intensity of which might even reach that of detonation itself.

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* *Comptes rendus*, 95 (1882), p. 1352. Summarised accounts are given in *Annales des Mines* (8), iv. 1883, p. 379. *Journal de Physique*, 1 (1882), p. 173; 4 (1885), p. 59. *Bull. Soc. Chim.* 39 (1883), p. 98 and 268.

The phenomenon was associated almost entirely with fast burning mixtures. In this connection they said : " *Cette pression très fugitive est d'autant plus grande que la vitesse de propagation est plus considérable. Elle peut devenir énorme, comme nous l'avons remarqué, avec l'onde explosive. . . . Ce sont précisément ces pressions passagères, sans relation directe avec le phénomène que nous voulions mesurer, qu'enregistrait notre appareil. Il se trouvait ainsi défectueux par l'exagération même des qualités qui nous l'avaient fait adopter.*" Mallard and Le Chatelier realised that the pressures developed in slow burning mixtures could be measured by this method quite accurately, without the interference of pressure waves. In such cases, however, unknown cooling losses would arise, and it was therefore decided to adopt another means of procedure.

Before describing this, however, it is of interest to recall how Dixon and Cain * made an attempt to measure the pressures developed in the explosion wave by determining the strengths of pieces of glass tubing which would either withstand or be shattered by the force of an explosion. Thus in the case of the detonation of the mixture $C_2N_2 + O_2$, the pressure exerted in the wave front was found to lie between 70 and 120 atmospheres, and with the mixture $C_2N_2 + O_2 + 2N_2$ between 63 and 84 atmospheres. The values obtained by Berthelot and Vieille for the effective pressures developed on explosion of similar mixtures in a closed vessel were only 25 atmospheres and 15 atmospheres, respectively, shewing the great difference between the transient and effective pressures in such cases. Moreover, as illustrating the extremely short duration of the high pressure attained in the detonation wave, the experiments † of W. A. Bone and B. Lean are of interest. It was found by them that the duration of luminosity of the explosion wave was less than $\frac{1}{5000}$th second, and much less than the time necessary for the shattering of a test tube attached to the end of the explosion coil employed.

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* *Mem. Proc. Man. Lit. Phil. Soc.* 1894, p. 174.

† *Brit. Assoc. Rep.* 1892.

In their later work Mallard and Le Chatelier employed a registering Bourdon-tube manometer, as illustrated in Fig. 93, which enabled them to measure not only the maximum pressure developed in an explosion but to trace a curve giving the pressure at any time during both the explosion and subsequent cooling periods.

The bomb (*A*), which was immersed in a water bath, was made out of sheet iron in cylindrical form (17 cm. in height and 17 cm. in diameter, with a capacity of 3·86 litres). Ignition was effected by an electric spark, the electrodes being placed centrally as in the earlier apparatus. The registering manometer consisted of a twisted tube (*C*), elliptical in section, which was filled either with water or glycerine. One end was closed and the other connected to the bomb. In an explosion the pressure developed, acting on the liquid, tended to straighten out the tube, thereby effecting a turning movement at the closed end (*D*), this being registered by means of a pen (*P*), which traced a curve on a piece of blackened paper wrapped round a rotating cylindrical drum (*B*). In this way pressure time records were obtained of a number of explosions of various mixtures both at atmospheric and lower initial pressures. A typical explosion record obtained in an explosion of cyanogen and air is shewn in Fig. 94. The wavy line (*A*) at the top was traced by a tuning fork, thereby enabling the accurate measurement of the relative rates of pressure development. It will be noticed how vibrations were set up in their indicator in the region of maximum pressure, owing to the inertia and comparatively long natural time-period of the Bourdon tube. Unfortunately such vibrations necessitated the adoption of certain corrections when interpreting the record, a source of error which has been avoided in most later researches.

Mallard and Le Chatelier's account of their work is of special interest on account of the careful study which was made of the pressure-time records. They deduced in the first place the laws governing the rates of cooling of various gaseous mixtures employed. In general, they adopted the formula $\frac{d\theta}{dt}=aT+bT^2$, where T = the temperature difference between the walls of the bomb and the explosion products at any moment. The coefficients a and b were not very different for the gases CO_2, O_2, N_2 and CO, and when the initial pressure was raised a remained constant but b diminished. The same type of equation was found to be equally applicable when steam was formed in the gaseous reaction, provided that there was a fair excess of diluent gas.*

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* The values for a and b in this case were, of course, of a different order.

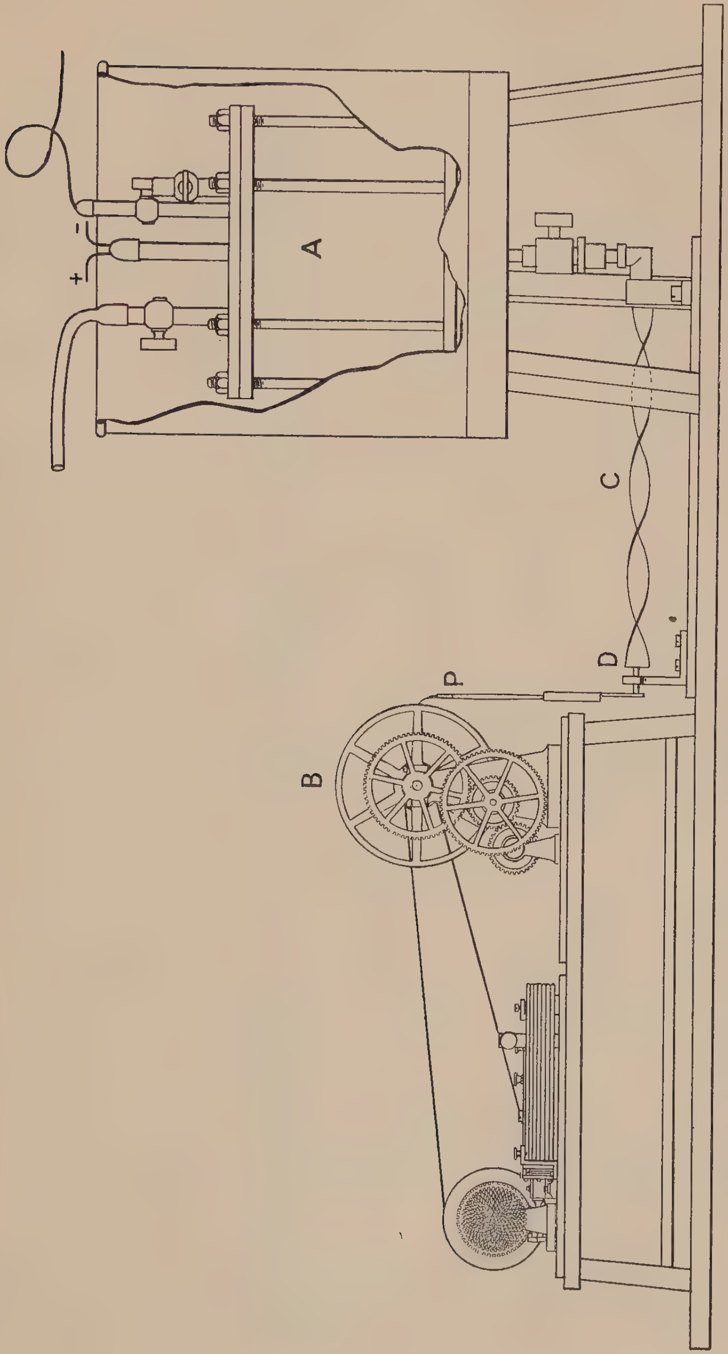

Fig. 93.—Mallard and Le Chatelier's Second Explosion Apparatus with Bourdon-tube Manometer.

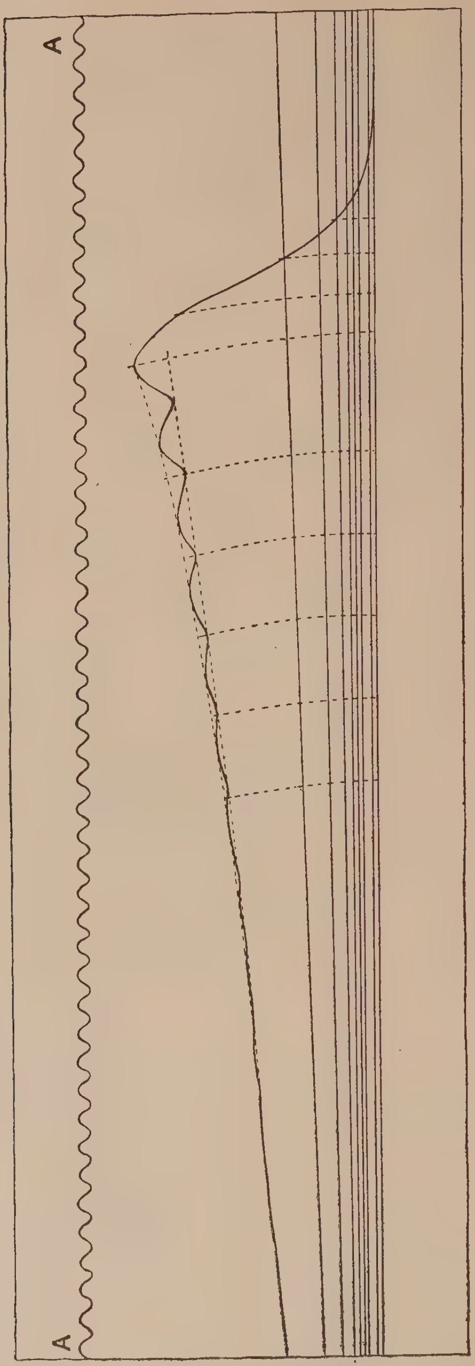

FIG. 94.—TYPICAL PRESSURE-TIME RECORD. (Mallard and Le Chatelier.)

When steam alone was formed (*i.e.* in a $2H_2+O_2$ explosion), the simple formula

$$\frac{dp}{dt}=a(P-P_0),$$

was adopted, where P=the pressure in the bomb and P_0=the vapour pressure at the temperature of the bomb.

Having made a thorough study of the cooling laws applying in each individual case, Mallard and Le Chatelier next proceeded to determine in which experiments, and to what extent, dissociation had occurred; for they argued that when dissociation occurs during an explosion heat must necessarily be evolved by recombination of the dissociated gases during the cooling period, as would be shewn by the rate of cooling for a limited time after the attainment of maximum pressure not conforming to the usual cooling laws. In the light of modern knowledge their deductions seem quite sound, for they found (*a*) definite evidence of the dissociation of carbon dioxide, the extent of the recombination depending on the initial pressure, (*b*) very little dissociation of water vapour—even at temperatures as high as 3300° C.—although it was admitted that the high rate of cooling in such experiments might mask such effects, and (*c*) little evidence of any dissociation of carbon monoxide at temperatures up to even 4000° C.

Finally, again using their formula for cooling, they were able to determine in each case a correction for the loss of heat during the attainment of maximum pressure. This was of a greater accuracy than that used by Berthelot and Vieille. Representative figures from their results are given in Table LVIII., p. 232, in which

P_i=the initial pressure in cm. mercury;

t_m=the time taken for the attainment of maximum pressure in seconds;

P_m=the maximum pressure attained in the explosion in cm. mercury;

P_m (corr.)=the said maximum pressure corrected by Mallard and Le Chatelier for cooling loss;

$\frac{P_m}{P_i}$ (corr.)=the ratio of the corrected maximum pressure to the initial pressure reduced to 0° and 760 mm.;

T_m=Mallard and Le Chatelier's estimate of the maximum temperatures attained in such explosions;

It may be observed how Mallard and Le Chatelier's results are in general agreement with those obtained by Berthelot and Vieille, particularly in regard to the influence of addition to electrolytic gas of one of the reacting gases as compared with that of nitrogen.

TABLE LVIII.—MALLARD AND LE CHATELIER'S EXPLOSION PRESSURES

Mixture.	P_i cm.	t_m sec.	P_m cm.	P_m(corr.) cm.	P_m/P_i (corr.)	T_m °C.
$2CO+O_2$	76	0·011	705	731	9·95	3130
$2CO+O_2+3CO_2$	74	0·118	462	485	7·04	1980
$2CO+O_2+4{\cdot}5CO_2$	77	0·360	370	449	6·12	1640
$2CO+O_2+2{\cdot}9CO$	73	0·033	509	519	7·40	1980
$2CO+O_2+2{\cdot}98O_2$	73	0·126	467	504	7·20	1920
$2CO+O_2+3{\cdot}0N_2$	73	0·138	469	505	7·21	1930
$2CO+O_2+4{\cdot}0N_2$	76	0·225	422	477	6·64	1670
$C_2N_2+O_2$	20	—	363	466	16·35	4190
$C_2N_2+O_2+3{\cdot}76N_2$	63	0·073	686	725	11·95	2500
$2H_2+O_2$	74	—	561	620	9·04	3380
$2H_2+O_2+1{\cdot}5O_2$	73	—	545	623	8·86	2830
$2H_2+O_2+6O_2$	73	0·0048	459	516	7·39	1970
$2H_2+O_2+1{\cdot}5H_2$	73	—	545	617	8·81	2800
$2H_2+O_2+6N_2$	73	0·0075	468	514	7·34	1960
$CH_4+2{\cdot}8O_2+10{\cdot}5N_2$	76	0·168	470	519	6·96	1660
$CH_4+2O_2+7{\cdot}24N_2$	76	0·058	608	646	8·93	2150

Mallard and Le Chatelier's Specific Heat Values

There remain for consideration Mallard and Le Chatelier's deductions for specific heats at high temperatures. Dealing with mixtures where it had been shewn that dissociation did not occur, they calculated a value of 13·6 for the mean molecular heat of carbon dioxide at 2000° C. and deduced the following formula for such values up to that temperature:

$$\overline{C}_v = 4{\cdot}33\,(T \times 10^{-2})^{0{\cdot}367}.$$

In the case of steam, the dissociation of which was considered to be negligible at temperatures up to 3350° C., they gave a value 16·6 at that temperature and deduced the formula:

$$\overline{C}_v = 5{\cdot}61 + 3{\cdot}28(T \times 10^{-3}).$$

In the case of the diatomic gases it was considered that their molecular heat capacities increase to the same extent over temperatures up to 3000° C., a conclusion which is now known to be approximately true. Thus they said: "*Les chaleurs spécifiques moléculaires des gaz parfaits, qui sont égales entre elles aux températures ordinaires, le sont encore aux températures élevées jusque près de 3000° C. et peut-être au dessus,*" and gave the following expression:

$$\overline{C}_v = 4{\cdot}8 + {\cdot}0006T.$$

It must here be stated that although such increase of specific heats with temperature was first predicted by Berthelot, actual priority of experimental verification of it was due to Mallard and Le Chatelier, whose work was quickly followed by that of Berthelot and Vieille. Mallard and Le Chatelier's formulae served for more than twenty years, and the general accuracy of their values is still reasonably good even in the light of recent advances in our knowledge of the subject.

Clerk's Experiments

Clerk's work falls in rather a different category from that of his French contemporaries, for he was primarily concerned with thermodynamical matters bearing upon the development of the gas-engine, and as most of his experimental results were concerned with coal gas-air mixtures they perhaps have less interest for chemists. Nevertheless, his general observations confirm those of the French workers and are of considerable importance.

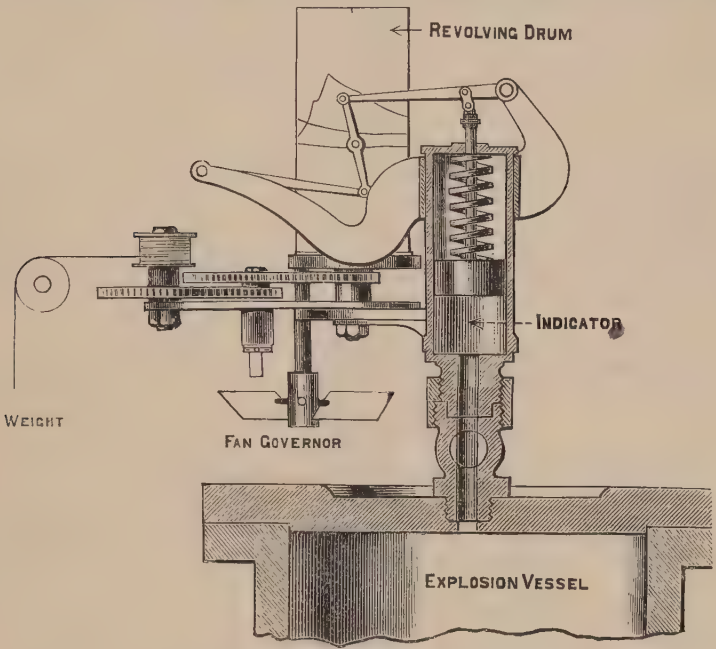

FIG. 95.—CLERK'S EXPLOSION APPARATUS.
(From Clerk's *The Gas, Petrol, and Oil Engine.*)

He communicated two notable papers to the Institution of Civil Engineers,* the first being a full account of the theory of the gas-engine, and the second a description of explosion experiments carried out during the years 1883–1884. His apparatus (illustrated in Fig. 95) consisted of a cylindrical explosion vessel 7 inches in diameter and 8¼ inches in length, thus having a capacity 317 cubic inches. To the upper cover was fitted a Richards indicator—functioning by means of a piston working against a spring—the general operation of which will be seen from the illustration. Of special interest are three pressure-time curves, reproduced in Fig. 96, obtained in explosions of (*a*) 1 volume of hydrogen to 6 of air, (*b*) 1 volume of hydrogen to 4 of air, and (*c*) 2 volumes of hydrogen to 5 of air. In the case of the richest mixture (*c*) it will be observed how oscillations were set up in the indicator spring, as in the case of Mallard and Le Chatelier's experiments. The pressures developed and the explosion times for these three mixtures are given in the following Table.

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* *Proc. Inst. Civil Engineers,* 69 (1882), p. 220; also 85 (1886), p. 1.

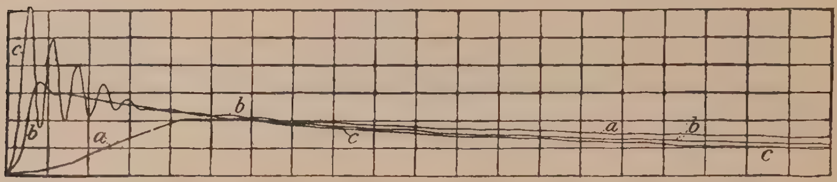

FIG. 96.—PRESSURE-TIME RECORDS OF HYDROGEN-AIR MIXTURES. (Clerk.)
(From Clerk's *The Gas, Petrol, and Oil Engine.*)

TABLE LIX.—EXPLOSIONS OF HYDROGEN-AIR MIXTURES (CLERK)

(At Atmospheric Pressure).

Mixture.		Maximum Pressure above atmos. in pounds per sq. in.	Calculated Maximum Pressure, assuming Constant Specific Heats.	Time of Explosion (sec.).
Hydrogen.	Air.			
1 vol.	6 vols.	41	88·3	0·15
1 vol.	4 vols.	68	124	0·026
2 vols.	5 vols.	80	176	0·01

Clerk's values were in substantial agreement with those of the French workers, and confirmed the fact that such pressures are only a fraction of those expected on ordinary calculations (as is shewn in Table LIX.).

All of Clerk's other experiments were made with coal gas-air mixtures, and are of interest as shewing the general change in the type of pressure-time record obtained as the mixture strength was varied. In Fig. 97 is shewn a series of such records and figures relating thereto are given in Table LX.

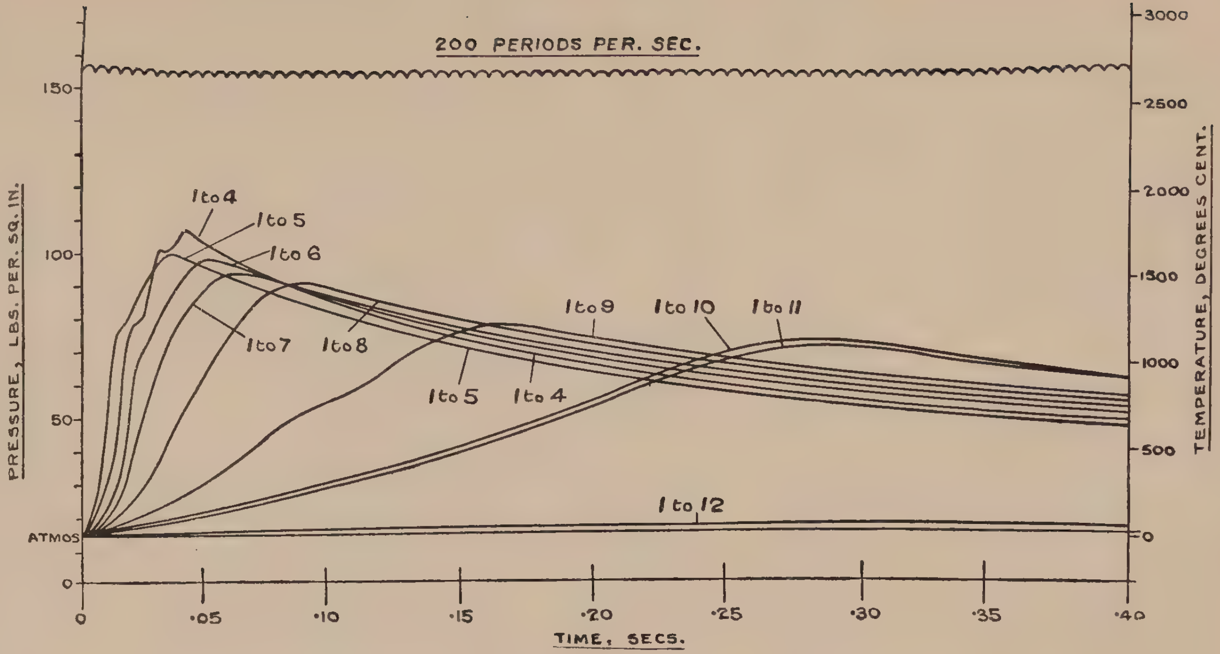

FIG. 97.—PRESSURE-TIME RECORDS OF EXPLOSIONS OF MIXTURES OF COAL-GAS AND AIR. (Clerk.)
(From Clerk's *The Gas, Petrol, and Oil Engine.*)

TABLE LX.—EXPLOSIONS OF COAL GAS-AIR MIXTURES (CLERK)

(At Atmospheric Pressure).

Mixture.		Maximum Pressure above atmos. in pounds per sq. in.	Time of Explosion (sec.).
Gas.	Air.		
1 vol.	11 vols.	58	0·290
1 vol.	10 vols.	60	0·305
1 vol.	9 vols.	65	0·155
1 vol.	8 vols.	77	0·087
1 vol.	7 vols.	80	0·067
1 vol.	6 vols.	85	0·055
1 vol.	5 vols.	87	0·042
1 vol.	4 vols.	93	0·045

It is of interest to note that in these experiments Clerk found that the highest pressure development was obtained when an excess of combustible gas was present.

As regards the problem of the 'missing pressure' in gaseous explosions Clerk put forward a further explanation; for at that time he thought Mallard and Le Chatelier's theory of increased specific heats at high temperatures to be erroneous, though he admitted the probable occurrence of dissociation at the maximum temperature. He considered that at the moment of maximum pressure only a fraction of the gas was actually burnt, even though the flame had completely filled the explosion vessel, and that combustion proceeded for a considerable time after its attainment. This may be termed the 'after-burning' theory.

It is well known that certain combustible gases, *e.g.* hydrocarbons and cyanogen, whose combustion involves a series of stages, are not wholly burnt 'at first brush,' and it is therefore possible that under certain conditions the later stages of combustion may not be completed until after the attainment of maximum pressure. And in other special circumstances, such as in the case of very dilute (slow burning) mixtures, this may also be the case. Nevertheless we doubt whether 'after-burning' can be considered as an invariable feature of gaseous explosions generally.

Summary

It has been shewn how in the early work on gaseous explosions in closed vessels, and in particular in that carried out during the years 1880–1885, it was definitely established that the pressures so developed were always considerably below those calculated on then known considerations. The great disparities between the found and 'calculated' maximum pressures have been attributed by various investigators to one or other of the following causes, namely:

1. *To the marked increases in the specific heats of steam and carbon dioxide with temperature.* This is now generally admitted to be one of the most important factors in such connection, and will be dealt with in greater detail in Chapter XXI.

2. *To loss of energy by direct radiation.* Thus in the explosion of a mixture of hydrogen and oxygen it seems probable that the initial action results in the formation of an intensely vibrating molecular complex from which steam issues as the first recognisable product. This subject has already been considered in Chapter XVIII., in relation to ordinary flames, and its bearing upon explosions in closed vessels will be considered in our next chapter.

3. *To dissociation of products (steam and carbon dioxide).* In the case of two combining gases producing a dissociable product, it is clear that if the average temperature of the system exceeds that at which dissociation begins, a percentage of the heat of combustion will not be available at the moment of maximum pressure.

4. *To heat lost by conduction.* This is not nearly so great as was supposed by Hirn, and is probably quite small in very fast burning mixtures.

5. *To the fact that combustion may not be completed within the period required for the attainment of maximum pressure, with the consequent occurrence of 'after-burning.'* In certain cases doubtless this factor is operative, but whether it is generally so, or counts much in the burning of turbulent mixtures, may be questioned.

No one cause by itself is capable of accounting for the observed facts, and all may play more or less important parts according to circumstances. Considerably more information on the subject has been forthcoming during the last twenty years, particularly that which was the outcome of the deliberations of the British Association Gaseous Explosions Committee (1907–1915), and with such work we shall deal in the next Chapter.

CHAPTER XX

FACTORS AFFECTING THE PRESSURES DEVELOPED IN GASEOUS EXPLOSIONS

The work of the Gaseous Explosions Committee of the British Association (1907–1915)

Whilst the researches of the earlier workers had focussed attention on the principal factors which govern the kinetic (pressure) energy development in a gaseous explosion, quantitatively very little was accurately known. The years 1907–1915 were, however, very fruitful in this respect, chiefly owing to the activities of the British Association Gaseous Explosions Committee; * for being constituted of all schools of scientific thought on the subject, it was able not only to collect the best available data but also to organise and initiate new researches into the problem. Such work included *inter alia* research upon (1) the direct measurement of explosion temperatures, (2) the influence of turbulence on the rate and magnitude of pressure development, (3) quantitative measurement of both radiation and cooling losses, (4) the estimation of the probable specific heats of gases at high temperatures. The reader particularly interested in this branch of the subject is recommended to consult the original reports, but for the purpose of this chapter a general outline will be given both of the work then carried out and of some more recent developments of it.

It may be pointed out in passing that unfortunately much of the work considered in this chapter has been carried out with mixtures of coal-gas and air; and while it is not denied that the general nature of phenomena associated with gaseous explosions can be demonstrated by the use of such mixtures, yet a settlement of fundamental issues in regard to gaseous combustion generally cannot be attained satisfactorily by the employment of so crude and complex a combustible. For combustion being essentially a chemical process, it is necessary that pure single combustible gases should be separately investigated. On this account it is satisfactory to note that in most recent research coal-gas is no longer employed.

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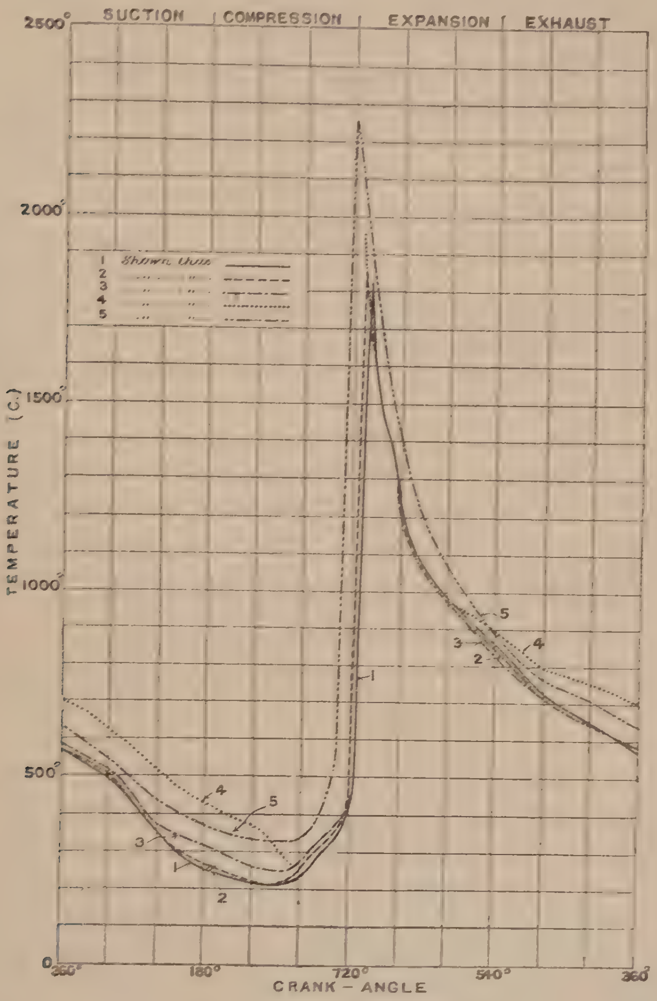
* *Reports of the British Association for the Advancement of Science*, 1908, p. 308; 1909, p. 247; 1910, p. 199; 1911, p. 130; 1912, p. 192; 1913, p. 166; 1914, p. 177; 1915, p. 158; 1916, p. 292.



	1	2	3	4	5
Ratio Air/Coal Gas * - -	7·35	7·08	7·13	6·71	5·66

FIG. 98.—TEMPERATURE CYCLE IN A GAS ENGINE. (Coker and Scoble.) (From *Proceedings of the Institution of Civil Engineers.*)

Direct Measurements of Explosion Temperatures

It would considerably lessen the difficulties experienced in considering gaseous explosions if one were able to make direct determinations of the temperatures attained therein, for at present we are only able to make approximate estimations of them from measurements of the pressure developments. Unfortunately the application of the only direct methods at present available, namely those using platinum-resistance thermometry or thermo-junctions, is limited to temperatures below the melting points of the platinum or platinum alloys employed.

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* Calorific value = 480 B.T.U. per cub. ft. (approx).

The first attempt to use a platinum resistance thermometer was made by Burstall in 1895, who then considered the highest temperature attained in an explosion of coal-gas and air to be 1250° C.* In 1901, however, he recorded 1570°, but such value was undoubtedly too low, for his platinum wire was unduly thick, causing much lag in recording the true temperature attained.† Some few years later Callendar and Dalby adopted an ingenious device whereby a delicate resistance thermometer fitted to a small gas-engine was shielded at the highest temperatures, and by measuring the temperature at different intervals during the compression stroke they were able to calculate the highest temperature, which was found to be between 2250° and 2500° C.‡

Undoubtedly the most successful attempt of all to measure, not only maximum temperatures but the temperature changes occurring in an engine-cycle, was that of Coker and Scoble.§ They employed a thermocouple, of wires (0·0005 – 0·0008 inches thick) composed of alloys of 10 per cent. rhodium-platinum and iridium-platinum, respectively, in conjunction with a short period Enthoven galvanometer. By this means instantaneous records of the changes occurring in a gas-engine cycle (shewn in Fig. 98) were obtained, and temperatures as high as 2250° C. recorded.

Thermal Equilibrium in Gaseous Explosions

Before leaving the subject of direct temperature measurement a series of experiments carried out by Hopkinson in 1906 is of considerable interest,‖ not so much because of the actual temperatures recorded but because of their demonstration of the nature of the temperature distribution at the moment of maximum pressure. Hopkinson employed a large dumpy cylindrical explosion vessel, shewn in Fig. 99, having a capacity of 6·2 cubic feet, ignition being at the centre (A). At B, C and D three rapidly acting platinum thermometers were placed, B being close to the spark, C at a distance of about 10 cm., and D about 1 cm. from the walls of the vessel. A pressure indicator was also fitted to the explosion vessel, both the pressure and temperature variations being recorded photographically on a revolving film.

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* *Phil. Mag.* 40 (1895), p. 282.

† *Proc. Inst. Mech. Engr.* 1901, p. 1031.

‡ *Proc. Roy. Soc.* A. 80 (1908), p. 57.

§ *Proc. Inst. Civil Engr.* 196 (1913), p. 1.

‖ *Proc. Roy. Soc.* 77 A. (1906), p. 387.

In the case of a 1 : 9 coal gas-air * mixture the maximum pressure was developed in about 0·25 second, this being less than $\frac{1}{30}$ second after flame had completely filled the vessel. At the moment of maximum pressure the distribution of temperature was roughly as follows :

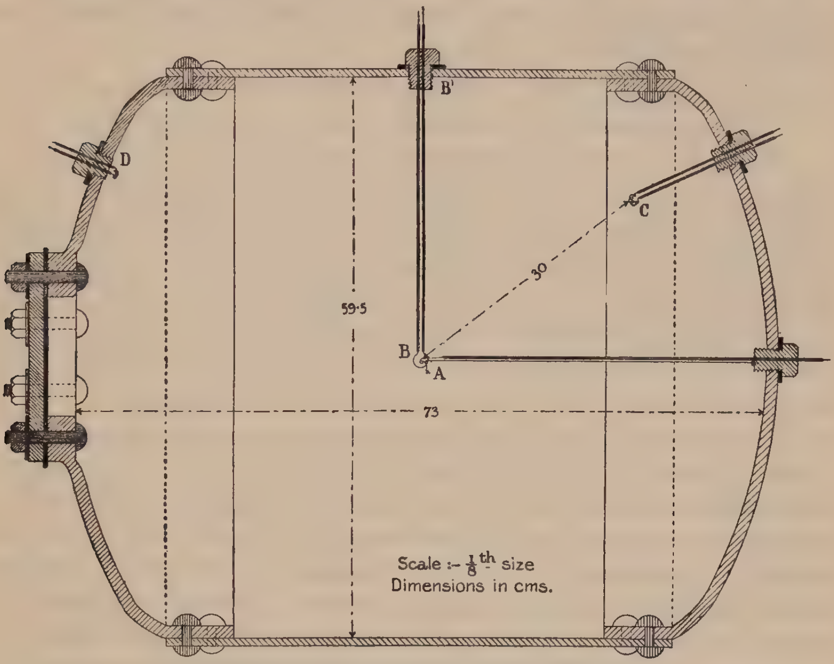

Fig. 99.—B. Hopkinson's Explosion Vessel.

	°C.
Mean (inferred from pressure) - - - - -	1600
(*a*) Centre near spark - - - - - - -	1900
(*b*) 10 cm. within the wall (*C*, Fig. 99) - - -	1700
(*c*) 1 cm. from wall at end (*D*, Fig. 99) -	1100 to 1300
(*d*) 1 cm. within wall at side - - - - - -	850

Commenting on these figures Hopkinson said, " At points *a*, *b* and *c* ; the gases can have lost but little heat at this time, and the differences of temperature are due to the different treatment of the gas at different places. At (*a*) it has been burnt nearly at atmospheric pressure, and compressed after burning to about six-and-a-half atmospheres absolute, while at (*c*) it has been first compressed to about six atmospheres as in a gas-engine, and then ignited without any subsequent compression. At the point (*d*) much heat has been lost, since this is the first point of the wall reached by the flame ; the gas here is ignited when the pressure is about two atmospheres, its temperature rises instantly to about 1300° C., and at once begins to fall.

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* The coal-gas had the composition H_2 = 47·2 per cent. ; CO = 7·15 per cent. ; CH_4 = 35·2 per cent. ; C_nH_m = 4·8 per cent. ; N_2 = 5·65 per cent.

"After combustion is complete, however, the motion of the gas set up by the explosion or by convection currents rapidly obliterated these initial differences." Thus, half a second after the attainment of maximum pressure, Hopkinson found:

Mean temperature (inferred from pressure) - - -	1100° C.
Mean temperature (shewn by the resistance of a long wire stretched from the centre to *D*, Fig. 99) - -	1160° C.

The explosion of a weaker mixture containing one volume of gas to twelve of air was found to differ markedly from that of the mixture just described, owing to the fact that the time taken for the attainment of maximum pressure (2·5 secs.) was now much longer, so that convection currents played an important rôle in the phenomenon; but even in this case Hopkinson found that the complete inflammation of the gas was nearly simultaneous with the development of maximum pressure. Indeed, he said "one-tenth of a second before maximum pressure there are undoubtedly places to which the flame has not spread, but it is extremely improbable that there are any such places one-tenth of a second after." Moreover, he opposed Clerk's 'after-burning' theory, asserting that at the moment of maximum pressure, or in the case of weak mixtures within a short interval afterwards, there was present in the explosion vessel 'a mass of CO_2, H_2O and inert gas in complete chemical equilibrium,' a conclusion which was afterwards generally accepted by the British Association Committee.*

Engine Indicator Diagrams

Although engineers are quite familiar with an ordinary indicator diagram, there may be some of our readers to whom a brief explanation of one may be of assistance (see Fig. 100).

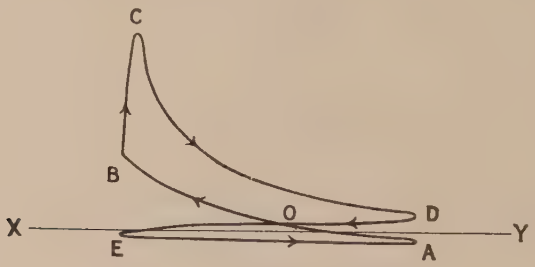

FIG. 100.—INDICATOR DIAGRAM.

The line is either traced by a pencil attached to the indicator, or recorded photographically by a beam of light reflected from a mirror operated by it. The diagram shows the pressure exerted in an engine cylinder at any moment during the cycle of operations. Thus at *A* the compression stroke is about to begin, and the line *AB* represents the rise in pressure as the piston travels towards the cylinder head. At a point occurring somewhere in the vicinity of maximum compression *B* the explosive mixture is ignited, and the pressure is thereby rapidly raised to *C* and afterwards falls until the end of the expansion stroke at *D*. *DE* represents the exhaust stroke and *EA* the suction stroke. At *A* the cycle of operations will commence again. *XY* represents the atmospheric pressure line, and it will be observed that on the suction stroke a pressure less than that of the atmosphere obtains. Taking the diagram as a whole, it is seen that the pressure at any point in the cycle is represented by the vertical height, and the cylinder volume in which such pressure is exerted is represented by the horizontal distance to the right of *B* (plus the clearance at the cylinder head). Moreover, the resultant work done during the cycle is represented by the area *DOBC* less the area *AEO*.

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* *First Report of Gaseous Explosions Committee*, 1908.

The Influence of Turbulence

It will be realised that there is a vast difference between the conditions prevailing when a gaseous explosive mixture is ignited in a closed vessel, in which it is perfectly ‘ stagnant,’ and when it is ignited in a gas engine; for in the latter case it has been rapidly sucked through an inlet valve and then compressed, and hence is in a state of considerable agitation. This fact accounts for the more rapid rate of pressure development in a gas engine explosion than in a ‘ static ’ explosion in which the same explosive mixture has been ignited. Such influence of turbulence was first observed by Schloesing and Montdesir [*] and its effect has been studied by a number of more recent workers.

Even in a gas-engine itself the nature of the pressure development is very largely affected by the degree of turbulence effected in the mixture. Some interesting experiments in this connection were carried out by Clerk,[†] who contrasted the nature of the pressure development, as shewn in an indicator diagram (see Fig. 101), when an explosive mixture was fired in a gas-engine under ordinary running conditions, and later, when, by ‘ tripping ’ the valves and allowing compression and expansion to proceed without ignition for two or three cycles, the former turbulent state had largely subsided. The effect was very marked, for when using a 1 : 9·3 coal gas-air mixture the line *A* to *B* (Fig. 101) represented the nature of the pressure rise under ordinary running conditions whereas the line A^1 to B^1 represented that when turbulence had largely subsided.

Other workers have studied the problem by fixing fans inside explosion vessels by means of gas-tight glands, and contrasting the pressure-time records obtained from the explosion of gaseous mixtures either in a stagnant condition without such fan working or in a turbulent state with it in operation. Generally speaking, explosive mixtures which under quiescent conditions develop pressure rapidly are but little affected by turbulence ; on the other hand, however, with slow burning mixtures its influence is considerable. The following figures obtained by Kratz and Rosecrans * for coal gas-air mixtures are typical of such effects.

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[*] *Vide* Mallard and Le Chatelier, *Ann. des Mines* (8), iv. (1883), p. 379.

[†] *Fifth Report Gaseous Explosions Committee, British Association Report*, 1912.

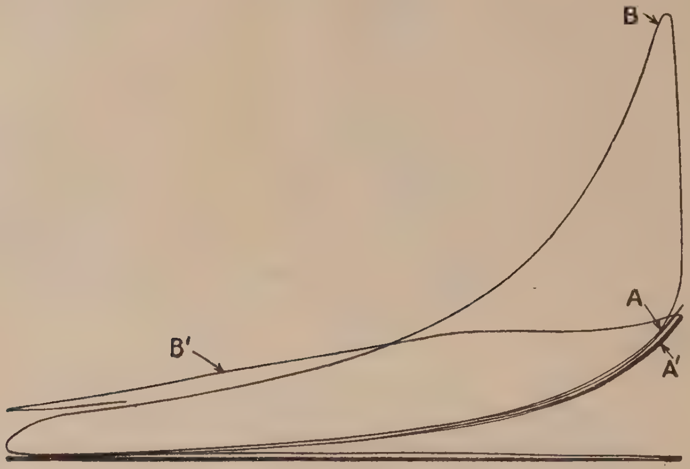

FIG. 101.—CLERK'S INDICATOR DIAGRAM SHEWING THE INFLUENCE OF TURBULENCE.

TABLE LXI.—INFLUENCE OF TURBULENCE ON COAL GAS-AIR EXPLOSIONS (KRATZ AND ROSECRANS)

(At Atmospheric Pressure).

Ratio Air/Coal-Gas.	$\frac{\text{P. Maximum}}{\text{P. Initial}}$.		Explosion Time (Milli-secs.).	
	With Turbulence.	Quiescent.	With Turbulence.	Quiescent.
2·08	6·92	—	70·0	—
2·61	7·23	6·44	28·0	95·0
3·13	7·48	6·68	39·0	71·0
3·65	7·24	—	38·0	—
4·17	6·70	6·30	51·6	83·0
5·21	6·13	5·52	49·6	139·0
6·25	5·53	4·70	81·0	329·0
7·29	4·84	3·76	136·0	942·0
8·33	3·15	—	344·0	—

* *Univ. Illinois Eng. Exp. Sta. Bulletin*, No. 133 (1922).

The Nature of Cooling Losses

The quantitative study of the energy-losses by radiation and conduction in a gaseous explosion is most difficult, and although the researches initiated by the British Association Committee have considerably added to our knowledge of the subject yet there is still much to be learnt. As far as conduction is concerned, it is generally conceded that the rate of heat flow from the hot gases per unit area of wall surface of an explosion vessel is dependent mainly on the temperature difference, the gas pressure and degree of agitation. Hence it may be concluded that the percentage heat loss by conduction in an explosion will decrease considerably as the size of the explosion vessel is increased, and, in fact, will be dependent in the main on its surface-volume ratio. At a temperature of a few hundred degrees the rate of cooling by conduction is considered to be proportional to the temperature difference between the hot gases and the walls of the explosion vessel. At higher temperatures, owing to the experimental difficulties encountered in such work, little data is available. According to David, however, with whose work we shall deal presently, the rate of cooling increases rapidly at higher temperatures, being proportional to the second power of the temperature difference at 1500°, and to as much as the fifth power at 2400°.

The question as to the loss due to radiation is not less complicated. It is generally accepted that the rate of heat loss for ‘ black-body ’ radiation is proportional to the fourth power of the temperature difference (Stefan's law), but as has been already mentioned in Chapter XVII. the radiation emitted in gaseous combustion largely occurs in well-defined bands, and the variation in the rate of radiation emission with temperature is therefore uncertain. With regard to the influence of the size of the explosion vessel on the radiation loss the experiments of Callendar, using Meker burners, are of considerable interest. He found, for example, that with one flame the radiation emitted was 68 units per sq. cm., but with a depth of six similar flames it rose to 282 units—thus shewing the ‘ surprising ’ transparency of the flame to its own radiation. It might be supposed that as gases under suitable conditions are capable of absorbing the radiations which they emit they would therefore be opaque to such radiation; but it must be remembered that the molecules are relatively far apart, and hence a large percentage of the radiation escapes.

From his observations Callendar arrived at the conclusion that the emission from a mass of radiating gas 100 cms. in depth at atmospheric pressure would be within half a per cent. of that from an infinite depth. If the pressure were increased to 20 atmospheres, the like emission would be obtained from a depth of 5 cms. only. David, however, has shewn that in explosions at atmospheric pressure the transparency is greater than that obtaining for flames. Moreover, he considered that the radiation loss per sq. cm. of wall surface for any given explosion in a cylindrical vessel l cm. in diameter and l cm. in length varied as $\sqrt{l}$. It is clear, therefore, that the radiation loss expressed as a percentage of the heat of combustion of the explosive mixture tends to become less important in very large explosion vessels.

Hopkinson's Experiments

In 1907 Hopkinson * published the details of an ingenious apparatus which he termed a " Recording Calorimeter for Explosions." It consisted of an explosion vessel made of a cast-iron cylinder one foot in diameter and one foot in length on to which were bolted two end plates. The cylinder was first completely lined with wood $\frac{1}{4}$-inch thick, and the end plates covered with pieces of cork. This lining was covered as completely as possible with a continuous piece of copper strip, the increase of electrical resistance of which during the progress of an explosion and subsequent cooling being recorded on a photographic film wound round a revolving cylinder. On the same film the pressure-time curve, A, was recorded by an optical indicator. A typical illustration of Hopkinson's record is shewn in Fig. 102, the wavy line, B, indicating the rise of temperature of the copper strip. By this means Hopkinson was able to record the quantity of heat taken up by the copper strip at any moment.† The procedure not only enabled a judgment to be formed of the nature of the cooling loss, but was also of assistance in forming an idea of the probable heat capacities of the gases concerned at high temperatures; for, knowing the heat of combustion of the original mixture fired and the amount of heat conducted away in the copper strip, an estimate can be made of the energy still in the gaseous products at any moment, temperature being inferred from the pressure-time curve. The method has been employed recently by Womersley with considerable success.‡ Hopkinson himself found in this way that

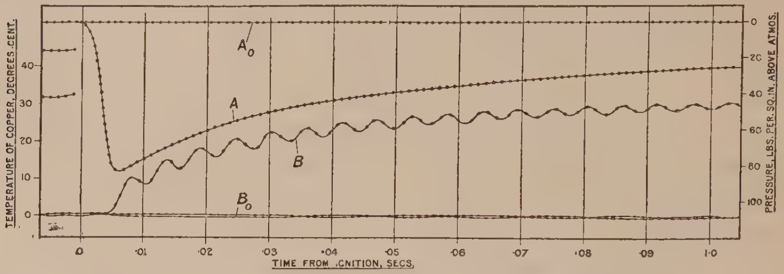

Fig. 102.—B. Hopkinson's Pressure and Heat-Loss Records.
(From Clerk's *The Gas, Petrol, and Oil Engine.*)

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* *Proc. Roy. Soc.* A. 79 (1907), p. 138.

† Making an allowance for the heat lost to the backing.

‡ *Proc. Roy. Soc.* A. 100 (1921), p. 483.

in the case of an explosion of a mixture of one volume of coal-gas to seven of air (see Fig. 102), the heat energy left in the explosion products one second after firing was in accordance with the mean specific heat values found by Holborn and Austin at the temperature (545° C.) then obtaining in the bomb, although 0·5 second after firing the value so calculated was not so concordant. Commenting on the rate of cooling loss Hopkinson said, " The heat loss begins about 0·05 second after ignition, when the flame first comes in contact with the copper. At first the loss goes on at a very great rate, and by the time the maximum pressure is reached, about 1700 calories, or 12 per cent. of the gross heating value of the gas, has passed to the walls. The rate of heat loss at this point is about 10 calories per sq. cm. per second, and the mean gas temperature is 1760° C. At 0·2 seconds from ignition the rate of heat loss is about 3·5 calories per sq. cm. per second, and the mean gas temperature 1300° C. This mean temperature is reduced in the ratio 74/100 between these two points, but the rate of heat loss at 0·2 seconds is only one-third of what it was at the maximum pressure."

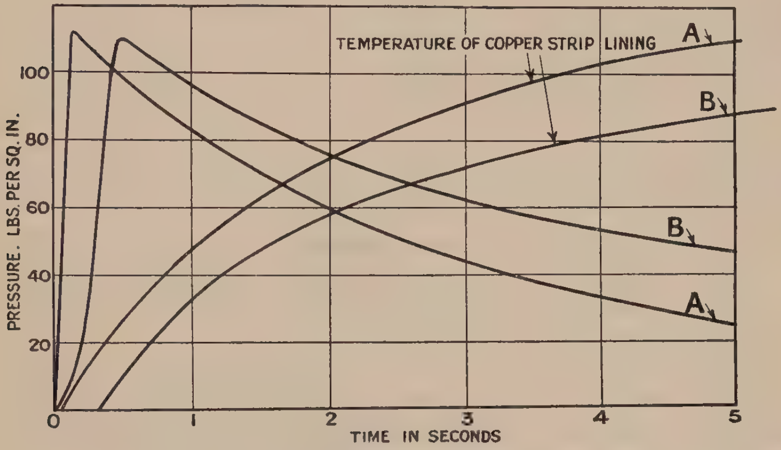

FIG. 103.—INFLUENCE OF TURBULENCE ON RATES OF PRESSURE DEVELOPMENT AND HEAT-LOSS. (Hopkinson.)

As illustrating the effect of turbulence both on the rate of pressure development and on the subsequent cooling period, Hopkinson fitted a fan to his explosion calorimeter with results of the type shewn in Fig. 103. For a 15 per cent. coal gas-air mixture the curves *A* represent the explosion with the fan running and *B* the explosion without it.

The Experimental Determination of Radiation Losses

In order to gain some information experimentally as to the quantitative nature and influence of the radiation emitted during a gaseous explosion Hopkinson carried out a series of experiments in a cylindrical cast-iron explosion vessel of 30 cms. diameter and 30 cms. in length, having its inside surface silver-plated.*

He first compared the pressure-time records obtained in this vessel (*a*) when the inside surface was highly polished, in which case about 95 per cent. of the total radiation would be preserved, and (*b*) when it was blackened over and the total radiation thus absorbed by the walls.

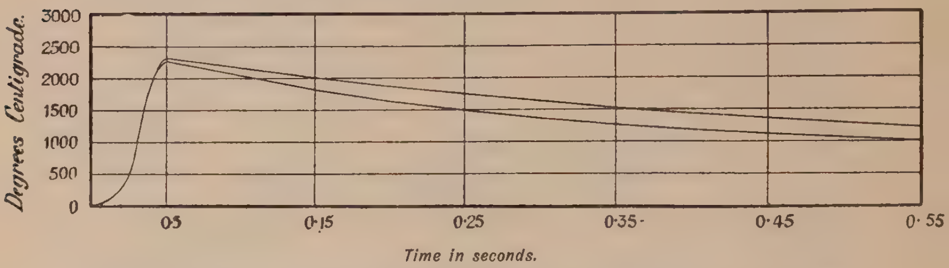

FIG. 104.—COMPARISON OF PRESSURE-TIME RECORDS OBTAINED WITH HIGHLY POLISHED AND BLACKENED WALLS. (Hopkinson.)

In Fig. 104 are shewn the two curves superimposed when a 15 per cent. coal gas-air mixture was exploded. After very many determinations carried out in this way he arrived at the conclusion that in case (*a*) the maximum pressure attained in the explosion was about 3 per cent. greater, and subsequently a much slower rate of cooling ensued, than in case (*b*), and he gave the following figures :

TABLE LXII.—COMPARISON OF EXPLOSIONS OF 15 PER CENT. COAL GAS-AIR IN A VESSEL (*a*) WITH HIGHLY POLISHED SURFACE, (*b*) BLACKENED SURFACE (HOPKINSON)

Max. Pressure (lbs./sq. in.).	Times after Ignition (sec.). Pressure (lbs./sq. in.).			
	0·15	0·25	0·36	0·45
(*a*) 114·0	98·7	84·2	73·5	64·9
(*b*) 110·8	89·2	73·1	61·3	53·5

Hopkinson also placed inside his explosion vessel a platinum strip bolometer and compared the rise in temperature in it (measured by its change of electrical resistance) when highly polished and when blackened. The following are representative of his experimental figures :

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* *Proc. Roy. Soc.* A. 84 (1910), p. 155.

Table LXIII.—Rise of Temperature of Platinum Strip (*a*) Highly Polished, (*b*) Blackened—placed inside an Explosion Vessel (Hopkinson)

Time from Ignition (sec.).	Gas Temp. °C.	Bolometer Temp. °C.		Ratio of Temperatures.
		Black.	Polished.	
0·05	2150	15·9	12·0	0·755
0·10	1940	45·8	31·9	0·695
0·15	1750	51·0	44·1	0·725
0·20	1590	70·0	51·7	0·74
0·30	1250	76·8	59·0	0·77
0·50	1030	78·7	62·5	0·795

In a later series of experiments David, then working with Hopkinson, fitted a fluorite window (which protected the blackened platinum bolometer) to the explosion vessel (as shewn in Fig. 105), and studied the rate of radiation emission during the whole course of an explosion. As, however, David has published many papers since that time we shall endeavour to give a brief summary of the principal features of his work as a whole.

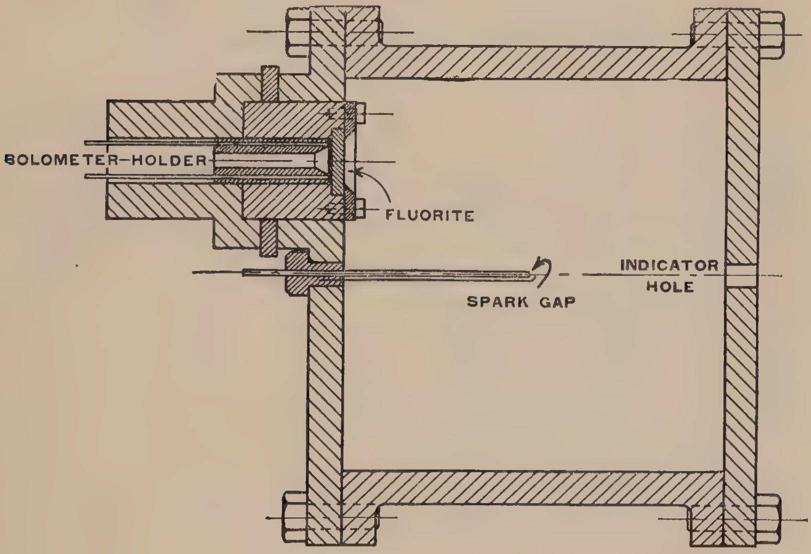

Fig. 105.—David's Apparatus.
(From the *Proceedings of the Institution of Mechanical Engineers.*)

He first examined the radiation loss occurring in coal gas-air mixtures of varying strengths, and arrived at the conclusion that the radiation emission was at a maximum before the attainment of maximum pressure, and was probably so when the flame filled the explosion vessel. The heat lost by radiation up to the moment of maximum pressure was found to be approximately proportional to the product of the third power of the maximum absolute temperature attained in the explosion and the time taken to attain the maximum pressure. The total heat lost by radiation throughout the explosion was found to be about 26 per cent. of the heat of combustion in a 15 per cent. mixture and about 23 per cent. in a 9·8 per cent. mixture. In the case of hydrogen-air explosions, however, the maximum rate of emission did not occur until the maximum temperature (pressure) was attained in the explosion, and the total radiation emitted throughout the explosion was 16·1 per cent. of the heat of combustion in the case of a 25·4 per cent. mixture, but only 8·2 per cent. in the case of a 10 per cent. mixture. As contrasting the results in the two cases David gave the following figures. It will be observed that in the case of the 25·4 per cent. hydrogen-air and 15·0 per cent. coal gas-air explosions almost identical maximum temperatures were attained.

TABLE LXIV.—COMPARISON OF RADIATION LOSSES IN HYDROGEN-AIR AND IN COAL GAS-AIR EXPLOSIONS (DAVID)

Strength of Mixture (Percentage Combustible in Air).	Maximum Temperature °C. (Inferred from Pressure).	Time of Explosion (sec.).	Total Radiation received by Walls.	Percentage Heat of Combustion lost by Radiation up to Maximum Pressure.	Percentage Heat of Combustion lost by Radiation during the Explosion and Subsequent Cooling Periods.
	Hydrogen-Air.				
25·4	2400	0·017	0·60	0·5	16·1
15·3	1580	0·065	0·245	1·3	11·0
10·0	1230	0·240	0·12	1·4	8·2
	Coal Gas-Air.				
15·0	2410	0·05	0·98	3·3	26·1
13·0	2170	0·07	0·81	3·7	25·0
9·8	1700	0·18	0·57	7·0	23·6

He also found that the radiation received by the walls of the explosion vessel during cooling after the explosion of coal gas-air mixtures varied very approximately as the fourth power of the absolute temperature of the gaseous mixture. As the radiation is known to consist of two bands with maxima at $2{\cdot}8\mu$ and $4{\cdot}4\mu$, it might have been expected that the radiation would have varied in accordance with Planck's formula for the mean wave length of about 3·5μ, which shews a variation more or less as the square of the absolute temperature. He pointed out that the fourth power loss as determined in his experiments is probably to be explained on the varying transparency of the hot gaseous mixture with temperature.

David also studied the influence of initial pressure on the percentage heat of combustion emitted as radiation in the case of a 15 per cent. coal gas-air mixture. As might be expected, he found this to decrease as the pressure was raised. This is shewn in Table LXV.

TABLE LXV.—INFLUENCE OF PRESSURE ON RELATIVE RADIATION LOSS (DAVID)

Time from Ignition (sec.).	Mean Temperature °C. inferred from Pressure.		Mean Radiation received cm^2. of Wall.		Total Heat Loss by Radiation, Percentage Heat of Combustion.	
	$P_i=\frac{1}{2}$ at.	$P_i=1\frac{1}{2}$ at.	$P_i=\frac{1}{2}$ at.	$P_i=1\frac{1}{2}$ at.	$P_i=\frac{1}{2}$ at.	$P_i=1\frac{1}{2}$ at.
0·05	2270	2400	0·061	0·14	3·3	2·5
0·10	2020	2210	0·2	0·425	11·0	7·7
0·15	1790	2040	0·29	0·615	15·9	11·3
0·20	1600	1890	0·35	0·75	19·2	13·6
0·25	1440	1765	0·39	0·843	21·4	15·3
0·50	1030	1350	0·47	1·065	25·7	19·3
0·75	810	1140	0·49	1·143	26·8	20·7
1·00	700	1010	0·492	1·158	26·9	21·0

By replacing the fluorite window, which transmits 95 per cent. of the total radiation emitted, with quartz,* which transmits 70 per cent. of the radiation between 2 and 3·5μ but is opaque to radiation of longer wave-length and more transparent to that of shorter length (or by plate glass which transmits 70 per cent. of that transmitted by quartz), David arrived at the following conclusion, " In explosions of coal-gas and air and of hydrogen and air the ratio of the energy in the 2·8μ radiation emitted to that of longer wave-length decreases as the temperature decreases. At about 1200° absolute the emission of wave-length 2·8μ decreases very rapidly, and with the temperature at 1000° absolute it is negligible. Radiation of longer wave-length than 2·8μ continues to be emitted even after the temperature has fallen to 900° absolute, though at this temperature the emission is small."

Recently † David has shewn that the rate of combustion of certain gaseous mixtures may be speeded up by passing infra-red radiation (produced by a heated nichrome wire) into them through a fluorite window. Thus, in mixtures of carbonic oxide and air the introduction of 4·6μ radiation, which is absorbed by carbonic oxide, speeded up combustion, though the introduction of other kinds of radiation had no effect. In methane-air mixtures the introduction of 3·2μ radiation, which is absorbed by methane, increased the rate of combustion. No similar effect was found in the case of hydrogen. When the nitrogen of the air was replaced by argon, oxygen, carbon dioxide or the combustible gas itself, the introduction of radiation into the reacting system appeared to have little or no effect. In Fig. 106, as illustrating the speeding-up effect of the introduction of infra-red radiation, the pressure time curves obtained on exploding a 25 per cent. carbonic oxide-air mixture are superimposed, N representing that obtained under normal conditions and R that when radiation was admitted immediately before and during combustion.

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* *Phil. Mag.* 39 (1920), p. 84.

† *Proc. Roy. Soc.* A. 108, 1925, pp. 618-627.

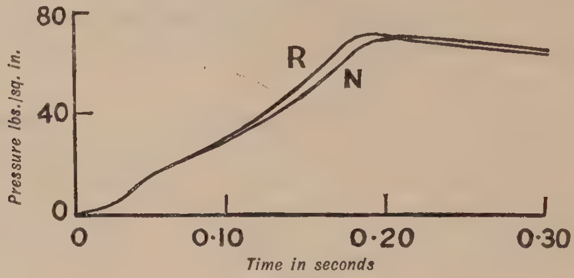

Fig. 106.

Heat Loss by Conduction

In 1920 David published the results of some experiments * which he had carried out in order to determine the heat loss by conduction as distinct from that due to radiation in coal gas-air explosions. For this purpose his explosion vessel was fitted with a highly polished silver grid mounted on a backing of linoleum and placed upon one of the end covers of his explosion vessel, as shewn in Fig. 107. The silver grid was connected with a reflecting galvanometer by means of which a curve was traced upon a revolving photographic film in the usual manner. With coal gas-air mixtures containing 15, 12·4 and 9·4 per cent. of coal-gas respectively the actual losses varied from about 27 to 37 per cent. of the heat of combustion. David further considered that the rate of loss of heat by conduction at 2400° absolute was proportional to the fifth power of the temperature difference between the explosion products and the walls of the vessel; at 2100° to the fourth, at 1800° to the third, at 1500° to the second, and probably at some lower temperature directly with the temperature difference. In Fig. 108 David has shewn the amount of the heat losses by both radiation (R) and conduction (C), also their sum (H) and the relative rates of such losses in curves R', C' and H'—in respect of

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* *Phil. Mag.* 40 (1920), p. 318.

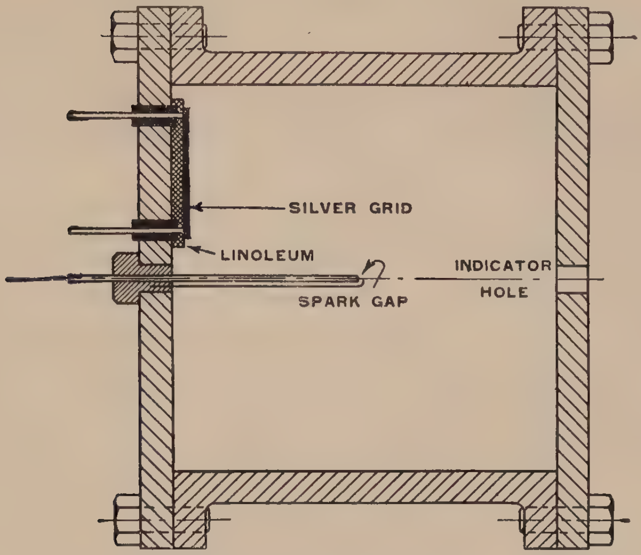

FIG. 107.—DAVID'S APPARATUS.
(From the *Proceedings of the Institution of Mechanical Engineers.*)

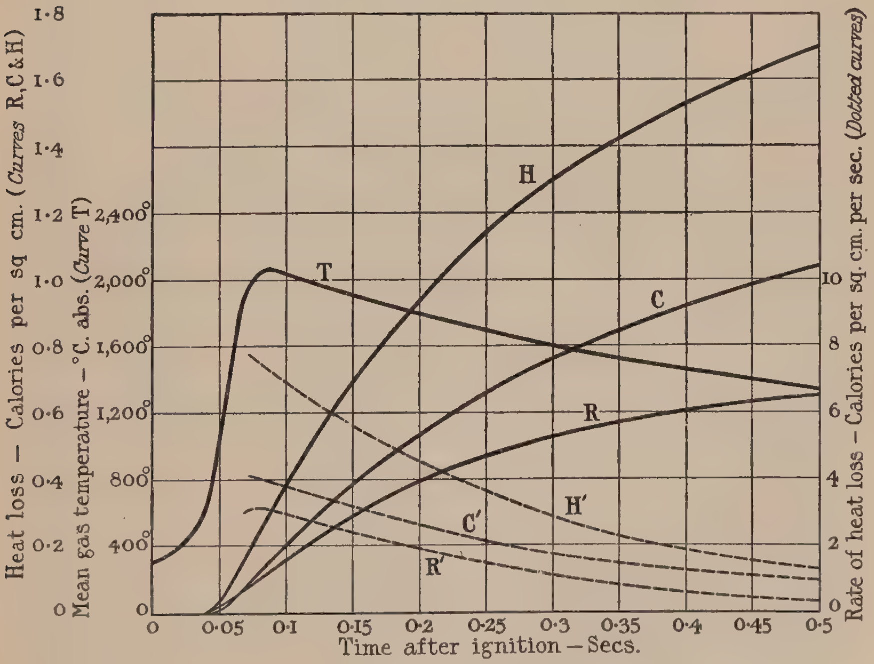

FIG. 108.—RELATIVE HEAT LOSSES IN THE EXPLOSION OF A 12·4 PER CENT. COAL GAS-AIR MIXTURE. (David.)

a 12·4 per cent. coal gas-air mixture. In Table LXVI. the corresponding numerical data are given:

TABLE LXVI.—RELATIVE HEAT LOSSES BY CONDUCTION AND RADIATION IN THE EXPLOSION OF A 12·4 PER CENT. COAL GAS-AIR MIXTURE AT ATMOSPHERIC PRESSURE (DAVID)

Time after Ignition (sec.).	Mean Gas Temperature (° Abs.).	Heat Loss per sq. cm. of Surface.			Heat Loss expressed as a Percentage of Heat of Combustion of the Coal-Gas.		
		Condⁿ.	Radⁿ.	Total.	Condⁿ.	Radⁿ.	Total.
0·08	2050 (Max. Temp.)	0·17	0·14	0·31	5·5	4·5	10·0
0·1	2030	0·21	0·18	0·39	6·8	5·8	12·6
0·15	1920	0·38	0·3	0·68	12·5	9·7	22·2
0·2	1800	0·53	0·4	0·93	17·4	13·0	30·4
0·25	1700	0·67	0·48	1·15	21·7	15·6	37·3
0·3	1610	0·77	0·53	1·30	25·0	17·2	42·2
0·3	1460	0·93	0·61	1·54	30·2	19·8	50·0
0·5	1330	1·05	0·66	1·71	34·0	21·4	55·0

Whilst such figures probably do indicate the general nature of the relative cooling losses by radiation and conduction, we think that the method of measuring conduction losses is perhaps open to the criticism that the polished silver grid could not be perfectly reflective, although other experiments carried out by David would appear to dispel any such doubt; and, secondly, that it cannot be considered that the heat received by a disc at any one position in an explosion vessel is representative of that being received by the walls of the explosion vessel as a whole. It must also be borne in mind that the relative radiation and conduction losses shewn refer only to such explosions carried out at atmospheric initial pressure and in a vessel of the size employed by David, for in larger vessels the radiation loss would become greater up to a certain limit in any case and might even exceed the conduction loss. At higher initial pressures, however, the radiation loss per unit of wall area would tend to become independent of the size of the explosion vessel and might therefore bear a constant relationship to the conduction loss.

Finally, from a knowledge of (*a*) the total heat loss to the walls of the explosion vessel up to the moment of maximum pressure, (*b*) the heat of combustion of the coal-gas in the mixture, and (*c*) the heat capacity of the gases, as inferred from that of the gaseous products of a stronger mixture similarly exploded and cooled down to the same temperature, David arrived at the following figures for the energy distribution at the moment of maximum pressure.

TABLE LXVII.—DISTRIBUTION OF ENERGY AT THE MOMENT OF MAXIMUM TEMPERATURE IN EXPLOSIONS OF COAL GAS-AIR MIXTURES (DAVID)

Mixture. Percentage Coal Gas in Air.	Heat of Combustion.	Internal Thermal Energy, *i.e.* Kinetic.	Available Chemical Energy.	Heat Loss to Walls of Explosion Vessel.
15·0	17,600	14,200 (81 %)	1,800 (10 %)	1,600 (9 %)
12·4	14,350	11,200 (78 %)	1,700 (12 %)	1,450 (10 %)
9·7	11,050	8,000 (72 %)	1,050 (9·5 %)	2,000 (18 %)

He considered that the figures so found for the available chemical energy at the moment of maximum pressure were accounted for by 'after burning'; whilst under his experimental conditions such factor may have been operative, we do not think that it provides the sole explanation, for without doubt dissociation must be allowed for, and there are other equally good alternative explanations, such as that of a different distribution of the total energy (as between vibrational, rotational and kinetic types) of steam and carbon dioxide molecules at their moment of formation at the maximum pressure from that appertaining to the same molecules when in true equilibrium at the same temperature. Indeed, many such factors may be collectively operative, and their true import will only be ultimately fathomed by a systematic study of the explosions of simple combustible gases rather than of such a complex mixture as coal-gas.

Clerk's Measurement of the Heat Capacity of a Gas-Engine Mixture at High Temperatures

It is not proposed at this juncture to deal with the probable volumetric heat capacities of gases at high temperatures, because calculations based on more recent explosion experiments have led to values of greater accuracy than those available at the time of compilation of the reports of the British Association Committee. Nevertheless, it seems desirable to mention here an ingenious method adopted by Clerk in 1905 for this purpose.* A gas-engine fitted with an indicator was employed. After firing an explosive mixture under normal running conditions, all the valves were then closed so that the explosion products were alternately expanded and compressed by the engine running on its own momentum. A diagram was obtained as shewn in Fig. 109. In the first compression the temperature of the gas rose to about 1100° C. (at the point *C*.). During the first three-tenths of the following expansion stroke (*CD*) the temperature fell to about 700° C. The work done in this part of the expansion was measured, and the heat loss, determined from a study of the curves, then added; in this way the change of internal energy corresponding to the temperature range

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* *Proc. Roy. Soc.* A. 77 (1905), p. 500.

1100° – 700° was obtained. It was considered that the volumetric heat capacity of the gaseous mixture over this range was, within the errors of experiment, equal to that at a mean temperature of 900° C. Values were similarly obtained at lower temperatures. As the results obtained refer only to the gas-engine mixture concerned we do not propose to give them here, but merely to draw attention to the ingenuity of the method.

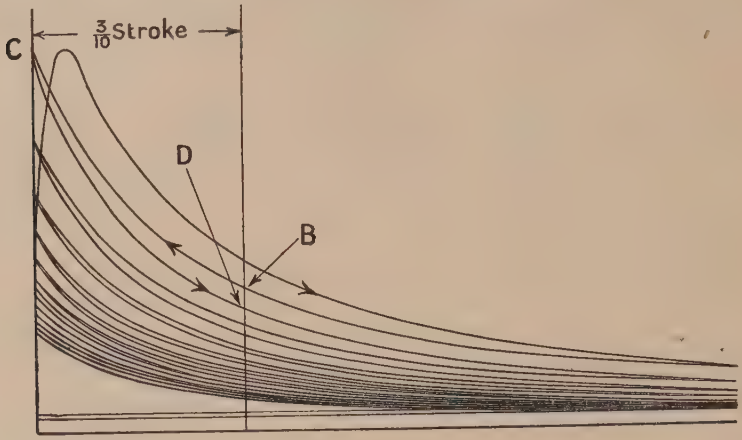

Fig. 109.—Indicator Diagram shewing Alternate Expansion and Compression of the Exploded Gases.

CHAPTER XXI

RECENT DETERMINATIONS OF EXPLOSION PRESSURES AND OF THE PROBABLE SPECIFIC HEATS OF GASES AT HIGH TEMPERATURES

Among the objects which have stimulated researches on gaseous explosions during the last twenty years, one of the most important has been that of determining the specific heats of gases and the degrees of dissociation of steam and carbon dioxide, respectively, at the maximum temperatures attained. At very high temperatures the measurement of the pressures developed in explosions affords the only available method for such work; and, although certain allowances have to be made for cooling losses, the results obtained have been found to agree well with those deduced theoretically from a knowledge of such values at low temperatures.* Excepting the work on gaseous explosions at high initial pressures carried out by Bone and his collaborators at the Imperial College, London, the results of which as bearing on specific heats will shortly be published, nearly all the recent work of this character has been carried out in Germany, the principal researches being those of Langen, and, later, of Pier, Bjerrum, Budde and Siegel, all working in Nernst's laboratory. In regard to the measurement of explosion pressures, the recent work of Fenning at the National Physical Laboratory, is also of importance.

Determinations of the Specific Heats of Gases at High Temperatures

The first work of importance undertaken after that of Mallard and Le Chatelier was that published by Langen in 1903.† He used a large bomb (Fig. 110) of 34 litres capacity in order to reduce cooling loss to a minimum. This was fitted for spark ignition at the centre and was also enclosed in a vessel through which water could circulate. The pressures developed were recorded by means of an ordinary engine indicator, but this did not permit of great accuracy owing to the inertia of its moving parts. He applied to his results a cooling correction of the type used by Mallard and Le Chatelier, and his corrected figures were in good agreement with those of the French workers.

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* For a complete discussion of the subject the reader is referred to the article by D. R. Pye on 'Specific Heats,' in Glazebrook's *Dictionary of Applied Physics*, vol. i.

† *Mitt. über Forsch.* 8, 1903; or *Ver. deut Ing.* 47,622 (1903). Vide *B.A. Rept. Gaseous Explosions Committee*, 1908.

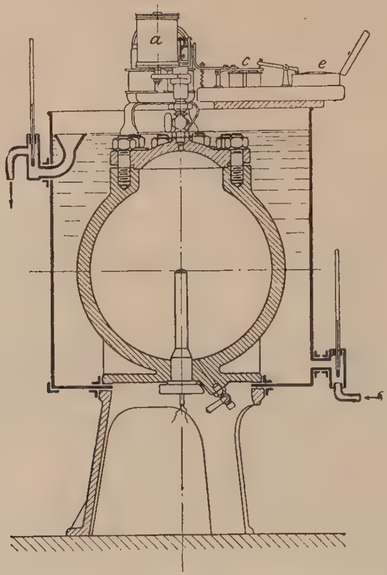

FIG. 110.—LANGEN'S EXPLOSION BOMB.

Langen's values for specific heats were probably too high, however, because he made no allowance for dissociation, and his cooling correction was probably too small; moreover, no allowance was made for loss due to radiation. Hence his results are now chiefly of historic interest, and need not be detailed here.

The work of Pier * and that of Bjerrum † was published between 1909 and 1913, but it did not come under the survey of the British Association Gaseous Explosions Committee, which dealt only with Langen's values and those obtained by Holborn and Henning.‡ Pier's apparatus (illustrated in Fig. 111) was of special interest because of its large capacity (35 litres), and the ingenuity of his recording manometer. He had previously endeavoured to use with doubtful success two other types of manometers, the first being of the moving piston type and the second a device by which he was able to record photographically the movement of a mercury column (in a

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* *Z. Elektro. Chem.* **15** (1909), p. 536; **16** (1910), p. 897; also *Zeit. Phys. Chem.* **62** (1908), p. 385; **66** (1909), p. 759.

† *Z. Elektro. Chem.* **17** (1911), p. 731; **18** (1912), p. 101; *Zeit. Phys. Chem.* **79** (1912), pp. 513 and 537; **81** (1913), p. 281.

‡ Holborn and Henning obtained specific heat values up to 1400° C., using a calorimetric method.

capillary tube) which by the development of the explosion pressure compressed an enclosed volume of methyl alcohol. His new manometer embodied in a different form the principle already applied for high pressure work by Petavel in 1905 (with which work we shall deal later on), namely, that of allowing the pressure developed in an explosion to work against a very strong spring, and magnifying, by optical devices, the resultant small movement. By such means inertia effects were reduced to a minimum, and pressure-time records were obtained quite free from effects due to oscillation set up in the manometer spring itself, except in the fastest burning mixtures. A typical example of his explosion pressure-time records is shewn in Fig. 112, from which it will be seen how completely ‘oscillation effects’ had been eliminated.

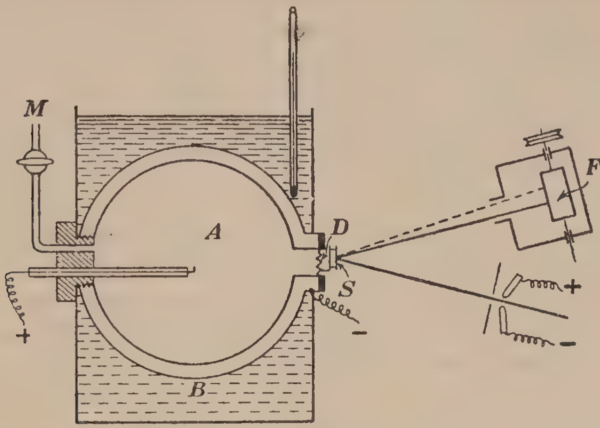

Fig. 111.—Pier's Explosion Bomb.
(From Partington and Shilling's *The Specific Heat of Gases*; Ernest Benn Ltd.)

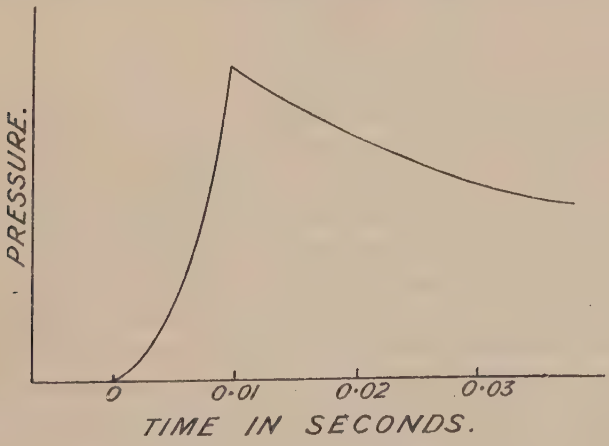

Fig. 112.—Typical Explosion Record. (Pier.)

His manometer was a circular corrugated steel disc (*D*) 0·1 mm. thick and 5 cm. in diameter firmly clamped down over an opening in his explosion vessel 3 cm. in diameter. The diaphragm was deflected 0·1 mm. per kilogram per sq. cm. pressure, and this was magnified about 100 times by having a small pointed brass rod at the centre of the diaphragm which moved a small mirror (*S*) fixed on a flexible plate. In later experiments Pier fixed the mirror to the diaphragm itself. A beam of light was thrown on to the mirror, which reflected it on to a photographic film wound round a revolving drum (*F*)—as shewn in the illustration. Calibration was effected by employing static gas pressures from a cylinder of carbon dioxide, but, owing to the risk of permanent distortion due to the time taken for attainment of pressure equilibrium in the large bomb, the disc was fitted temporarily to a small 20 c.c. vessel for this purpose. It may be stated here that such discs can be used with a high degree of accuracy, and that they are now largely employed for engine-indicators as well as for closed-vessel explosion work at initial pressures not greater than a few atmospheres.

Pier exploded various mixtures at an initial pressure of one atmosphere, and as the attainment of maximum pressure generally occurred in less than 0·01 second he considered that for all practical purposes he need add no cooling correction, a supposition which was later shewn by Bjerrum to be unwarranted.

The explosion temperatures were calculated by means of the formula :

$$T_m = \left(\frac{P_m}{P_1} \times \frac{1}{r} - 1\right)(273 + T_i) + T_i,$$

where T_i = initial temperature,
T_m = explosion temperature,
P_i = initial pressure,
P_m = maximum pressure,
r = ratio of the number of molecules in the products to that in the initial mixture.

He first set out to test the validity of the supposition that the molecular heat capacity of argon (being a monatomic gas) is constant and independent of temperature. This he was able to do by exploding mixtures of oxygen and hydrogen, containing excess of hydrogen in order to suppress dissociation, with a definite excess of argon. By exploding such mixtures at different initial temperatures, and calculating in each case the heat capacities of the steam and argon, he found no reason to suppose that the heat capacity of argon had deviated from a constant value of 2·98 calories per gram. molecule.

In order to determine the heat capacity of nitrogen, he adopted the procedure of determining the relative quantities of nitrogen and argon which when added to a hydrogen-oxygen mixture developed the same temperature. Such method (he supposed) would avoid within limits any error due to cooling and radiation losses, which would be practically the same in each case.

The heat capacity of carbon dioxide could not be determined by means of the explosion of carbon monoxide-oxygen mixtures, owing to the comparatively slow rate of flame propagation and consequent appreciable cooling loss in such explosions. For this reason he exploded theoretical acetylene-oxygen mixtures diluted with nitrogen, carbon dioxide, or excess oxygen.

In this way the following equations were developed for the mean molecular heats at constant volume over a range of temperatures up to about 2300° C.:

$$\text{Nitrogen } \bar{C}_v = 4{\cdot}900 + 0{\cdot}00045\,t.$$

$$\text{Hydrogen } \bar{C}_v = 4{\cdot}700 + 0{\cdot}00045\,t.$$

$$\text{Carbon dioxide } \bar{C}_v = 6{\cdot}800 + 3{\cdot}3 \times 10^{-3}t + 0{\cdot}95 \times 10^{-6}t^2 + 0{\cdot}1 \times 10^{-9}t^3.$$

$$\text{Steam } \bar{C}_v = 6{\cdot}065 + 0{\cdot}0005t + 0{\cdot}2 \times 10^{-9}t^3.$$

Bjerrum's work was carried out with the primary object of measuring the dissociation of steam and carbon dioxide at high temperatures. He employed Pier's apparatus, but ignited explosive mixtures not only at atmospheric pressure but also at pressures as low as 0·1 or 0·2 atmosphere in order to promote such dissociation. He also deduced cooling corrections to be added to the pressures recorded experimentally; for as the initial pressure was raised such loss was diminished, and by determining the relative amount of inert gas to be added in similar experiments at different initial pressures, so that the temperature obtained in each case was the same, he was able to form an idea of relative losses at each pressure. It was found that in Pier's explosions of hydrogen-oxygen mixtures at atmospheric initial pressure a cooling correction of about 1·8 per cent. should be made, and in his own experiments at about $\frac{1}{7}$ atmosphere initial pressure a correction of as much as 14 per cent. was necessary.*

The degrees of dissociation were deduced by observing the difference in the pressures (temperatures) developed when theoretical ($2H_2 + O_2$ or $2CO + O_2$) mixtures were exploded first with addition of nitrogen, and then with a corresponding addition of one of the reacting gases so as to suppress dissociation. For, according to the principle of mass action, the dissociation of a gas such as carbon dioxide (or steam) is a reversible transaction, as follows: $2CO_2 \rightleftharpoons 2CO + O_2$,

and the relation between the concentration of a gas and that of its dissociated products is represented at any one temperature by an equilibrium constant K. In the case of the dissociation of carbon dioxide,

$$K = \frac{[CO]^2[O_2]}{[CO_2]^2}.$$

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* The cooling loss was in fact found to be inversely proportional to the initial pressure.

Obviously, therefore, addition of excess of either carbonic oxide or oxygen to a theoretical $2CO + O_2$ mixture must cause an increase in the equilibrium concentration of carbon dioxide at the maximum explosion temperature.

For steam Bjerrum found the following relation for the equilibrium constant K:

$$\log K = 2{\cdot}79 - \frac{24193}{T}$$

applying over a temperature range of 2600°–3000° absolute.

From a knowledge of the dissociation constant the specific heat values at high temperatures could be calculated, and by using these in conjunction with those of Pier he developed formulae,* based upon the distribution of energy in a complex molecule according to the quantum theory, by means of which the mean volumetric heat capacities of the various gases could be calculated with a high degree of accuracy up to a temperature of 3000° C.

The values for the mean volumetric heat capacities (calories per gram molecule) summarised by Bjerrum are as follows:

TABLE LXVIII.—MEAN MOLECULAR HEAT CAPACITIES OF GASES AT HIGH TEMPERATURES (AS SUMMARISED BY BJERRUM)

Nitrogen.		Steam.		Carbon Dioxide.	
°C.	Cals. ¶	°C.	Cals. ¶	°C.	Cals. ¶
0° to 200° †	4·73	110° to 620° †	6·51	0° to 200° †	7·48
,, to 630° †	4·91	,, to 1000° †	6·95	,, to 630° †	8·6
,, to 1000° †	5·25	,, to 1327° †	7·40	,, to 1000° †	9·33
,, to 1347° †	5·31	,, to 1811° ‡	7·92	,, to 1364° †	9·84
18° to 1519° ‡	5·43	,, to 2110° ‡	8·54	,, to 1611° ‖	9·98
,, to 1783° ‡	5·58	,, to 2377° ‡	9·37	,, to 1839° ‖	10·28
,, to 1951° ‡	5·79	,, to 2663° §	10·00	,, to 2110° ‖	10·47
,, to 2182° ‡	5·87	,, to 2908° §	10·50	18° to 2714° §	10·9
,, to 2367° ‡	5·93	,, to 3064° §	10·90		

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* Bjerrum's theoretical formulae are as follows:

Hydrogen. $\bar{C}_v = \frac{5}{2}R + R\phi[2{\cdot}0\mu]$.

Oxygen, *Carbonic Oxide*, *Nitrogen* $\bar{C}_v = \frac{5}{2}R + R\phi[2{\cdot}4\mu]$.

Carbon Dioxide. $\bar{C}_v = 3R + 2R\phi[5{\cdot}0\mu] + R\phi[8{\cdot}1\mu]$.

Steam. $\bar{C}_v = 3R + 2R\phi[1{\cdot}3\mu] + R\phi[3{\cdot}6\mu] + \left(\frac{T}{3100}\right)^4$,

where $$\phi(\lambda) = \frac{1}{2}\frac{\frac{\beta C}{\lambda T}}{e^{\frac{\beta C}{\lambda T}} - 1} + \frac{1}{2}\frac{\frac{\beta C}{2\lambda T}}{e^{\frac{\beta C}{2\lambda T}} - 1},$$

C = velocity of light; λ wave-length of infra-red absorption band; and $\beta C = 14{,}580$.

† Holborn and Henning. ‡ Pier (recalculated by Bjerrum).

§ Bjerrum. ‖ Pier. ¶ per gram molecule.

The values given in Table LXVIII. have been plotted in Fig. 113 so that the reader may appreciate the general order of the rise of mean molecular heat capacities with temperature, of the gases referred to. The actual values, however, although fairly accurate, should not be considered as final and will no doubt ultimately require some modification.

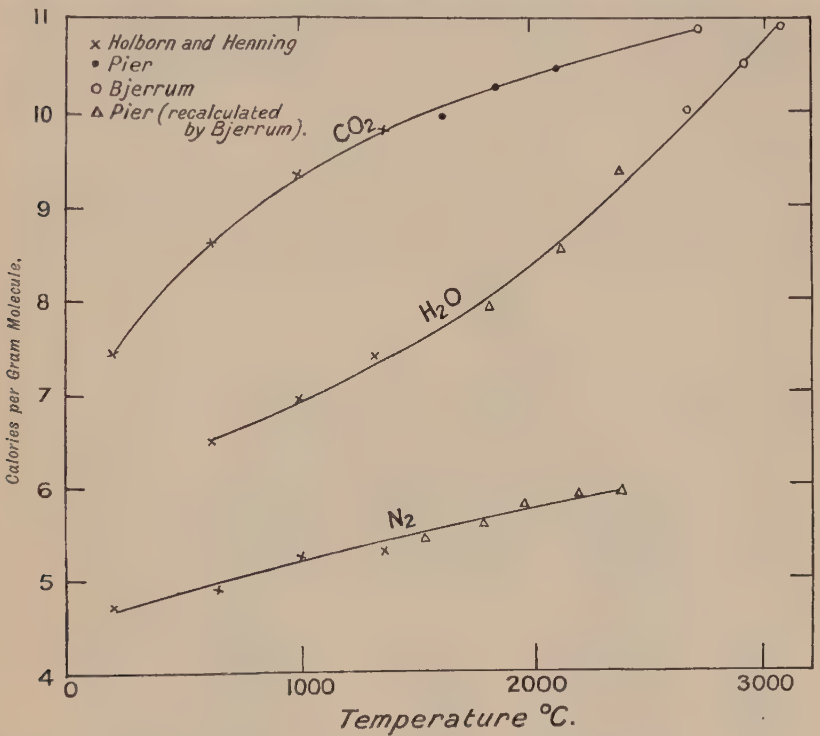

Fig. 113.—Mean Molecular Heat Capacities. (Bjerrum.)

Bjerrum's estimation of the percentage dissociation of steam and carbon dioxide at high temperatures and at atmospheric pressure was as follows:

Table LXIX.—Dissociation of Steam and Carbon Dioxide at High Temperatures and 1 Atmos. Pressure (Bjerrum)

	Steam.					
Temperature (abs.)	2300°	2642°	2698°	2761°	2834°	2929°
Percentage dissociation	2·6	4·3	7·5	8·6	9·8	11·1
	Carbon Dioxide.					
Temperature (abs.)	2640°	2879°	2900°	2945°	3116°	
Percentage dissociation	21·0	51·7	49·2	64·7	76·1	

The results for carbon dioxide are not considered to be as accurate as those for steam, owing to the high order of the necessary cooling corrections. It is important to bear in mind that the above figures for dissociation are estimated for atmospheric pressure only.

The influence of pressure upon such dissociations may be predicted from the knowledge that in a reversible system any change in the factors of equilibrium (*e.g.* temperature, pressure and active masses) from outside must be followed by a reverse change inside the system. Thus a rise of temperature will cause the equilibrium to shift in the direction of heat absorption; and, similarly, if there is a change in the number of molecules in the reaction, increase of pressure will effect a shift of the equilibrium in the direction of decreasing volume. Therefore, in the cases of the dissociation of steam and carbon dioxide, where the reversible systems $2CO \rightleftharpoons 2CO_2 + O_2$ and $2H_2O \rightleftharpoons 2H_2 + O_2$ are operative, increase of pressure at any one temperature will diminish dissociation. Thus, for example, the following data for the dissociation of steam and carbon dioxide, respectively, at various temperatures and pressures have been deduced from experimental results by Nernst and Wartenburg and by Bjerrum.*

TABLE LXX.—DISSOCIATION OF STEAM AND CARBON DIOXIDE.

Pressure (Atmospheres).	0·1.	1·0.	10.	100.
Temp. (Abs.).	Steam.			
1500°	0·043	0·02	0·009	0·004
2000°	1·25	0·58	0·27	0·125
2500°	8·84	4·21	1·98	0·927
3000°	28·4	14·4	7·04	3·33
3500°	53·1	30·9	16·1	7·79
	Carbon Dioxide.			
1500°	0·104	0·0483	0·0224	0·0104
2000°	4·35	2·05	0·96	0·445
2500°	33·5	17·6	8·63	4·09
3000°	77·1	54·8	32·2	16·9
3500°	93·7	83·2	63·4	39·8

In 1914 a further paper on specific heats of gases at high temperatures was published by Siegel,† who exploded various hydrogen-oxygen mixtures using the apparatus employed by Pier and Bjerrum. He improved the experimental technique so that initial pressures up to two atmospheres could be employed, considering that by this means cooling loss would be very small. A cooling correction deduced similarly to that of Bjerrum was applied, but Siegel criticised Bjerrum's calculations on the ground that such cooling correction should not be added to the pressure (temperature) but be deducted from the heat of combustion in any particular case, because by correcting (and thereby raising) the temperature the deduced specific heat values would apply to temperatures which were probably never actually attained. Siegel also made allowance for the dissociation of the hydrogen molecule itself at high temperatures.

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* See, however, the concluding paragraph of this chapter.

† *Zeit. Phys. Chem.* 87 (1914), p. 641.

Pier's formulae were corrected, on the grounds outlined above, as follows :

Mean molecular heat for oxygen and nitrogen from 0° to T° abs.,

$$\overline{C}_v = 4{\cdot}850 + 0{\cdot}000375T\ ;$$

for hydrogen $$\overline{C}_v = 4{\cdot}650 + 0{\cdot}000375T.$$

Siegel's steam formula, whilst applying accurately at high temperatures is not in agreement with known values at low temperatures and need not be given here.*

Fenning's Experiments

Fenning has studied the explosion of mixtures of various combustible gases and vapours with air or oxygen at initial pressures up to 10 atmospheres, and at initial temperatures up to 400° C. His explosion vessel (shewn in Fig. 114) was cylindrical in shape, being 7 inches in diameter and

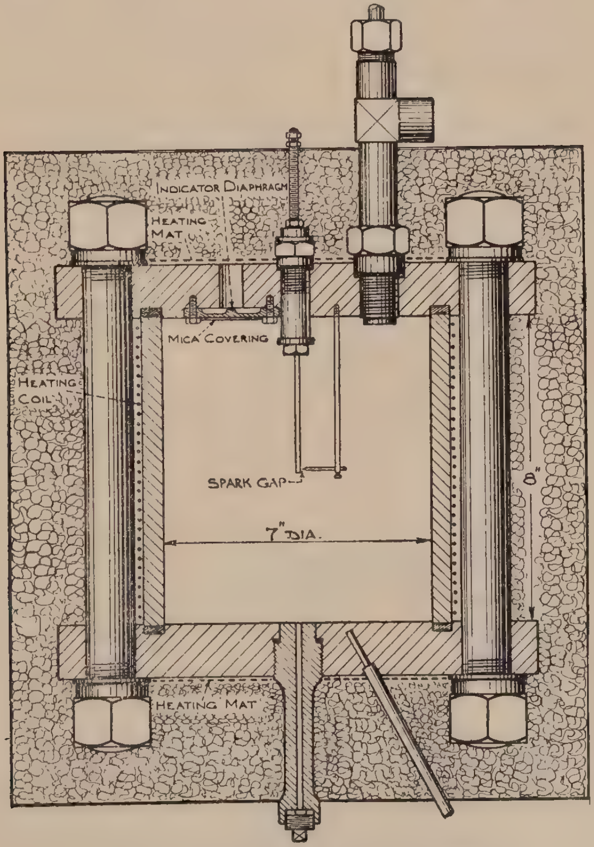

FIG. 114.—FENNING'S EXPLOSION VESSEL.
(From *Rep. and Mem. Aeronautical Research Committee.*)

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* The reader desirous of studying the subject further is recommended to refer to Partington and Shilling's *Specific Heats of Gases*, Ernest Benn Ltd.

8 inches long. It could be heated by means of a nichrome wire winding mounted on mica, the temperature being recorded by means of three thermocouples set in pockets drilled at different positions in the walls. The sparking plug was specially designed to be gas-tight after being heated to 500° or 600° C.

The indicator (Fig. 115) consisted essentially of a solid rimmed plane diaphragm, 0·07 in. in thickness and $1\frac{1}{2}$ ins. in diameter, fitted flush with the inner surface of the explosion vessel, and protected from heating effects by a mica covering. To the centre of the diaphragm a steel wire was fitted, which transmitted the deflections to a mirror lever, similar in principle to that designed by Petavel. The mirror lever was itself kept in position by a second steel wire, the tension of which could be adjusted as desired. Such a manometer was capable of giving a high degree of accuracy, but in very fast explosions the mirror lever was found to be susceptible to vibrations set up in the steel wires. The pressure-time records were made in the usual way on very rapid sensitised paper, the moment of sparking being also recorded by means of a secondary spark gap, in series with the ignition gap, which was placed near the recording paper.

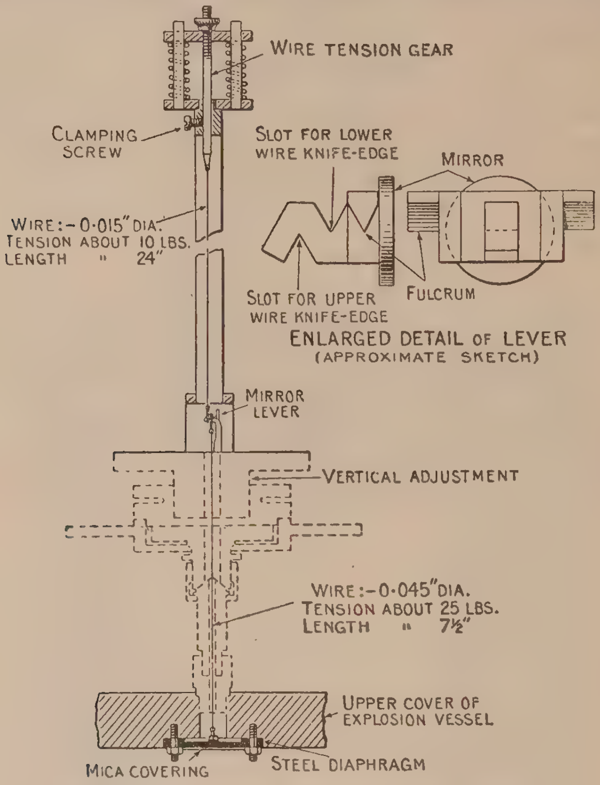
WIRE TENSION GEAR
CLAMPING SCREW
SLOT FOR LOWER WIRE KNIFE-EDGE
MIRROR
WIRE:-0·015" DIA. TENSION ABOUT 10 LBS. LENGTH " 24"
SLOT FOR UPPER WIRE KNIFE-EDGE
FULCRUM
ENLARGED DETAIL OF LEVER (APPROXIMATE SKETCH)
MIRROR LEVER
VERTICAL ADJUSTMENT
WIRE:-0·045"DIA. TENSION ABOUT 25 LBS. LENGTH " 7½"
UPPER COVER OF EXPLOSION VESSEL
MICA COVERING
STEEL DIAPHRAGM

FIG. 115.—FENNING'S RECORDING MANOMETER.

Following up the observations of Bone and Haward * (to which reference will be made in the next chapter), that hydrogen exerts a remarkable influence in speeding up the rate of pressure development in carbon monoxide-air explosions at high initial pressures, Fenning made similar experiments under conditions of temperature and pressure comparable with those obtaining in gas-engine practice. His results are in remarkable agreement with those carried out at high pressures, where, however, the effect referred to is more marked. Two mixtures were first of all made of hydrogen and air and carbon monoxide and air, each in the proportions required for complete combustion and in a state of comparative dryness. These were then blended in different proportions and time-pressure records obtained of the explosions of each such mixture. The numerical results are summarised below in Table LXXI. :

TABLE LXXI.—THE EXPLOSION OF H_2-CO-AIR MIXTURES (FENNING)

Initial Temperature—50° C. Initial Pressure—76·8 lbs./sq. in.

Experiment No.	Mixture.		Maximum Pressure lbs./sq. ins.	Time taken for the Attainment of Maximum Pressure (sec.).	
	H_2-Air. Per cent.	CO-Air. Per cent.		From Spark.	From Rise of Pressure.
1	100	—	564	0·0075	0·0059
2	49·7	50·3	564	0·0155	0·0123
3	24·8	75·2	563	0·0293	0·0239
4	11·9	88·1	563	0·0465	0·0383
5	8·0	92·0	562	0·0566	0·0482
6	4·1	95·9	559	0·0759	0·0645
7	2·2	97·8	557	0·1002	0·0860
8	0·2	99·8	542	0·2457	0·2048

The pressure-time records obtained in the above experiments, which bring out very well the remarkable influence of hydrogen upon a CO-air explosion, are reproduced in Fig. 116.

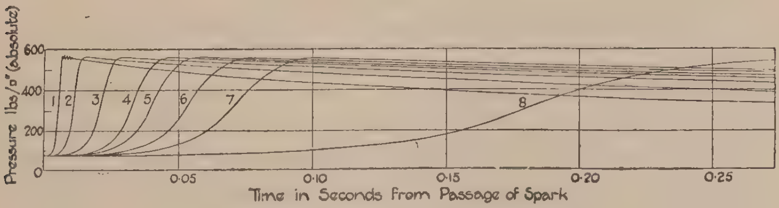

FIG. 116.—PRESSURE-TIME RECORDS OF THE EXPLOSION OF H_2-CO-AIR MIXTURES. (Fenning.)

(From *Rep. and Mem. Aeronautical Research Committee.*)

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* *Proc. Roy. Soc.* A. 100 (1921), p. 67.

In Fig. 117 are shewn the pressure-time records obtained when carbonic oxide-air mixtures were exploded with various additions of water vapour. In this connection Fenning said, "the addition of 0·3 volumes of water vapour to 100 volumes of comparatively dry CO-air mixture reduced the explosion time from about 0·29 to 0·16 second, whereas an addition of 1·68 volumes was associated with an 'explosion time' of about 0·095 seconds." The mixture, saturated with water vapour under the experimental conditions (50° C. and 78·6 lbs. per sq. in.), and containing 2·38 volumes per cent., attained its maximum pressure slightly quicker, in 0·090 second. Comparing the relative influences of hydrogen and water-vapour, respectively, in speeding up the combustion of carbonic oxide-air mixtures Fenning found that the addition of 2·2 per cent. of a theoretical hydrogen-air mixture had the same influence as the addition of 1·21 per cent. of water vapour; in other words, 0·63 per cent. of hydrogen had the same effect as 1·21 of water vapour in such connection. This result was in conformity with the conclusions of Bone and Haward with regard to CO-air explosions at much higher initial pressure.

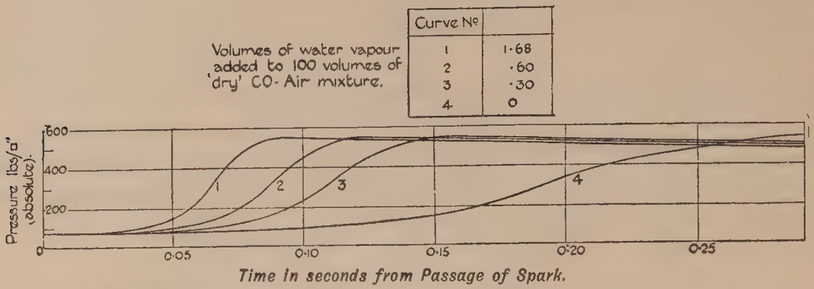

FIG. 117.—INFLUENCE OF WATER VAPOUR ON THE EXPLOSION OF A CO-AIR MIXTURE. (Fenning.)
(From *Rep. and Mem. Aeronautical Research Committee.*)

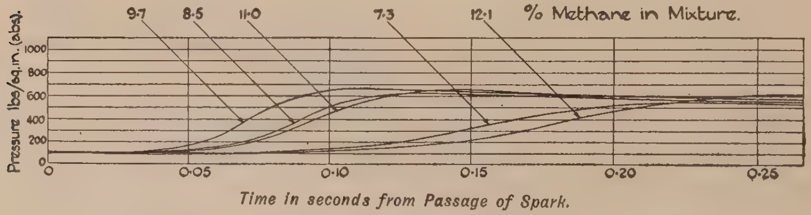

FIG. 118.—THE EXPLOSION OF METHANE-AIR MIXTURES. (Fenning.)
(From *Rep. and Mem. Aeronautical Research Committee.*)

Fenning also made an extensive study of methane-air explosions. In the first instance he investigated the effect of mixture-strength by exploding mixtures of composition varying between 7·3 and 12·1 per cent. methane, at 100° C. and at an initial pressure of

95 lbs. per sq. ins. Typical pressure-time records obtained in this series of experiments are shewn in Fig. 118, and the numerical data as to ‘ explosion time ’ and ‘ explosion rise ’ recorded graphically in Fig. 119. Mixtures containing from 9·7 to 10·5 per cent. of methane gave about the same pressure rise on explosion, whereas the ‘ explosion time ’ was a minimum in the region of the 9·7 per cent. mixture. Thus the fastest burning mixture and those developing the highest pressure contained a small excess of methane above that required for complete combustion, a result in accordance with general experience and accountable on the principle of mass action.

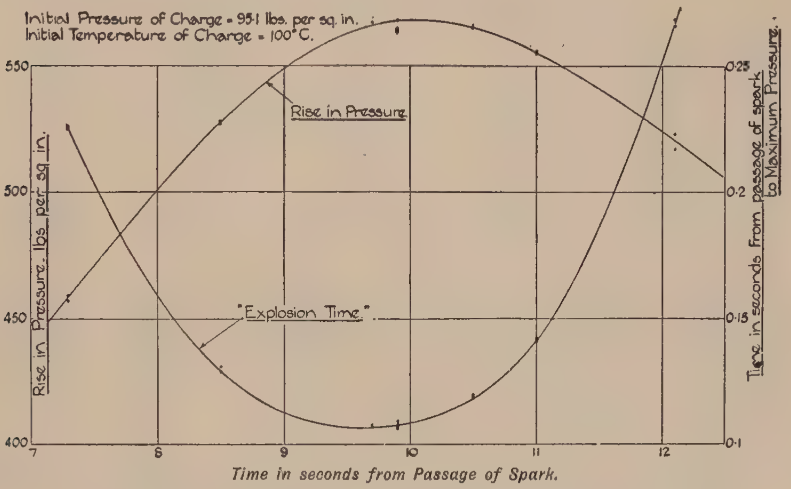

Fig. 119.—The Explosion of Methane-Air Mixtures. (Fenning.)
(From *Rep. and Mem. Aeronautical Research Committee.*)

In the case of the explosion of hydrogen-air mixtures at an initial pressure and temperature of 16·6 lbs. per sq. in. and 50° C. respectively, the following figures were obtained :

Table LXXII.—Hydrogen-Air Explosions (Fenning)

Percentage H_2 in Mixture.	Maximum Pressure. lbs./sq. ins.	Time taken for the Attainment of Maximum Pressure (sec.).	
		From Spark.	From Rise of Pressure.
34·7	112	0·0070	0·0051
32·4	113	0·0072	0·0052
30·4	115	0·0076	0·0055
28·7	112	0·0084	0·0058
28·0	111	0·0087	0·0067
26·5	110	0·0094	0·0071
25·2	108	0·0103	0·0073

And, as illustrating the part played by the diluent in the explosion of electrolytic gas mixtures, the following are taken from Fenning's figures :

TABLE LXXIII.—INFLUENCE OF DILUENTS UPON EXPLOSIONS OF ELECTROLYTIC GAS (FENNING)

Initial Temperature 20° C. (approx.).

Mixture (Approximate Composition).	Initial Pressure. lbs./sq. in.	Maximum Pressure. lbs./sq. in.	Time taken for the Attainment of Maximum Pressure (sec.).	
			From Spark.	From Rise of Pressure.
$2H_2+O_2$	29·8	275	0·00072	0·00044
$2H_2+O_2+2N_2$	30·2	261	0·0023	0·0017
$2H_2+O_2+4N_2$	29·4	235	0·0055	0·0047
$2H_2+O_2+2O_2$	29·1	255	0·0016	0·0011
$2H_2+O_2+4O_2$	29·1	224	0·0029	0·0022
$2H_2+O_2+2H_2$	29·4	269	0·0010	—
$2H_2+O_2+4H_2$	29·3	237	0·0019	—
$2H_2+O_2+2CO_2$	29·7	211	0·0046	0·0038
$2H_2+O_2+4CO_2$	29·4	166	0·0255	0·0206

From the point of view of gas-engine practice it is important to compare the pressure development in gaseous explosions under varying conditions of initial pressure and temperature. Fenning has done this for theoretical hydrogen-air * and methane-air mixtures over the range of the usual working conditions of gas- and petrol-engines.

TABLE LXXIV.—INFLUENCE OF INITIAL TEMPERATURE AND PRESSURE ON A 28·8 PER CENT. HYDROGEN-AIR MIXTURE (FENNING)

Initial Temperature °C.	Initial Pressure. lbs./sq. in.	Maximum Pressure lbs./sq. in.	$\frac{P_m}{P_i}$.†	Time of Attainment of Maximum Pressure (sec.).	
				From Spark.	From Start of Rise.
54	16·6	112	7·53	0·0084	0·0058
52	41·7	296	7·87	0·0068	0·0052
55	78·0	567	8·13	0·0061	0·0051
102	19·0	114	7·51	0·0076	0·0054
101	48·0	302	7·87	0·0063	0·0046
99	89·7	581	8·08	0·0063	0·0049
199	24·1	113	7·05	0·0064	0·0045
199	60·7	304	7·57	0·0057	0·0042
199	112·8	585	7·86	0·0050	0·0042

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* *Rep. and Mem.* No. 902 *Aeronautical Research Committee*, 1924.

† These values in order to be comparable amongst themselves are corrected as follows : $\frac{P_m-(P_i-P_i\text{ corrd.})}{P_i\text{ corrd.}}$, where P_i-corrd. = the initial pressure corrected to 15° C.

His results with a 28·8 per cent. hydrogen-air mixture are shewn in Table LXXIV. The initial temperature was varied between 54° C. and 300° C., but without doubt at the highest temperature a certain amount of ‘ slow combustion ’ occurred, and on this account the results have been omitted from the table. The range of initial pressures employed was between 16·6 lbs./sq. in. and 112 lbs./sq. in.

Similar experiments were made with a 9·9 per cent. methane-air mixture. In this case temperatures up to 400° C. and pressures up to 171·5 lbs./sq. in. were employed, with results as shewn in Table LXXV.

TABLE LXXV.—INFLUENCE OF INITIAL TEMPERATURE AND PRESSURE ON A 9·9 PER CENT. METHANE-AIR MIXTURE (FENNING)

Initial Temperature °C.	Initial Pressure lbs./sq. in.	Maximum Pressure lbs./sq. in.	$\frac{P_m}{P_i}$.*	Time of Attainment of Maximum Pressure (sec.).	
				From Spark.	From Start to Rise.
24·7	30·3	252	8·57	0·0997	0·0778
24·6	53·0	446	8·65	0·1163	0·0963
100	38·1	259	8·51	0·0798	0·0614
100	66·7	460	8·62	0·0933	0·0812
100	95·0	660	8·71	0·1090	0·0918
200	48·2	270	8·57	0·0628	0·0525
200	84·4	477	8·64	0·0750	0·0669
200	120·6	684	8·69	0·0838	0·0726
300	58·2	273	8·36	0·0496	0·0405
300	102·3	486	8·48	0·0597	0·0512
300	145·9	701	8·57	0·0671	0·0591
400	68·5	282	8·30	0·0410	0·0360
400	120·1	495	8·30	0·0473	0·0408
400	171·5	719	8·46	0·0548	0·0465

It is thus apparent that in both cases, the effect of raising the initial temperature at a given pressure was to diminish the time required for the attainment of maximum pressure, a result which might be anticipated, seeing that in such explosion the rate of flame propagation probably depends largely upon ‘ conduction ’ of heat from layer to layer of the medium. No general conclusion can be drawn from the experiments, however, as to the influence of pressure, a subject which will be dealt with in a later chapter.

It should be stated that, whilst this volume was in the press, Fenning and Tizard communicated to the Royal Society the results of some new experiments on the dissociation of carbon dioxide in explosions which had shewn Bjerrum's results to be too high. Thus, for example, they had found a 62 per cent. dissociation at 3300° abs. and atmospheric pressure as against the 7·5 per cent. given by Bjerrum.

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* See footnote to Table LXXIV.

CHAPTER XXII

GASEOUS EXPLOSIONS AT HIGH PRESSURES

So far we have considered phenomena associated with gaseous explosions in closed vessels at relatively low initial pressures only. In recent years investigations have been made—chiefly at the Imperial College of Science and Technology, London—into explosions at high initial pressures, which have disclosed new features of considerable interest to chemists. As, however, it is hardly possible adequately to deal with this new branch of research within the limits of a single chapter, arrangements have been made for the early publication of a supplementary volume upon it in conjunction with Dr. D. M. Newitt. Therefore, in the present chapter, we will confine ourselves to an outline only of some of the principal results to date.

So many recent developments in other fields of investigation have shewn what an important part pressure *per se* may play in chemical interactions—*e.g.* the production of ammonia from its elements and that of methyl alcohol, etc., from carbonic oxide and hydrogen by high pressure catalysis are outstanding instances—that chemists would hardly be surprised if in gaseous explosions high pressures were likewise to effect new results in some cases. And, apart altogether from purely chemical or thermodynamical factors, the physical consequences of high pressure, as for example radiation effects, may be considerable. For inasmuch as the chief difference between the conditions of high and low pressure experiments lies in the absolute concentration of the interacting molecules, it may be expected that factors whose operations chiefly depend on such concentration will become more dominant as the pressure rises. Indeed, the value of high-pressure work lies in the fact that it tends to show up and accentuate the operations of factors the influence of which may be either masked or overlooked at ordinary pressures.

It might be anticipated that *inter alia* the following influences will be operative in high-pressure explosions, namely :

(1) Generally speaking, an increase in the density of the explosive medium, involving, as it does, a proportionate increase in the number of

molecular collisions per second, would cause an increase of the absolute amount of chemical change in a given volume per second; and, if such increased rate of combustion is proportionally greater than the increase in the density of the medium, the time taken for the whole volume of gas in the enclosure to combine would be diminished. Such, indeed, is generally the case, carbonic oxide-air explosions being a conspicuous exception owing to other special circumstances supervening.

(2) The rate of heat losses would become relatively less, and consequently the maximum temperature and pressure attained would become greater as the density of the medium increases. Such consideration would certainly apply to losses by ‘conduction,’ and probably also to those due to ‘radiation’ because of the increasing opacity of the medium as its density increases.

(3) As the pressure increases the effects of ‘dissociation’ would diminish, though here it must be remembered that, inasmuch as any increase in the maximum temperature would have an opposite effect, what is actually observed in any particular case will be the *resultant* of these two effects. Actually, where carbon dioxide is concerned, the pressure effect outweighs that of temperature; but, where steam is concerned, the two effects seem nearly to balance.

(4) An increase in the density of the medium may affect both the emission and absorption of radiant energy during an explosion; and, as radiation is now known to play an important rôle in ‘activating’ molecules, new reactions may become prominent in high-pressure explosions which are hardly noticeable at lower pressures. This is certainly so in carbonic oxide-air explosions, as will be seen later.

Researches at the Imperial College, London

We will now outline some of the principal results which have accrued up to date from researches carried out in recent years chiefly upon explosions of hydrogen-air, carbonic oxide-air, and methane-air mixtures (or of corresponding mixtures in which the nitrogen was replaced by its equivalent volume of some other diluent such as argon, helium, oxygen, etc.) at various initial pressures up to 175 atmospheres. They were begun twenty years ago by W. A. Bone and his collaborators at the University of Leeds, and, after being suspended during the War, they were resumed in 1919 at the Imperial College, London, with the assistance of the late W. A. Haward until the unfortunate accident which ended his life in December 1920. Since 1921 they have been continued there in conjunction with Drs. D. M. Newitt and D. T. A. Townend. The heavy capital costs of the expensive apparatus required have been defrayed out of a series of grants made by the Government Grants Committee of the Royal Society and of the Department of the

Scientific-Industrial Research, to whom all thanks are due. The results have been published by the Royal Society.*

Apparatus and Methods. The gases employed in the experiments are prepared, purified and then separately stored in 10 cub. ft. gas holders, from whence they are separately compressed into steel cylinders under pressures up to 200 atmospheres. The experimental explosive mixtures are always made up in one or other of the various explosion bombs a few minutes before firing them.

It is necessary to carry out all such explosions in specially designed vessels of forged steel capable of withstanding the sudden development of very high explosion pressures, which in some cases have been nearly 2000 atmospheres; also, the method of measuring and recording them must be capable of following accurately, and with the least possible lag, a rise in pressure from (say) 50 to 500 atmospheres occurring within $\frac{1}{200}$th of a second.

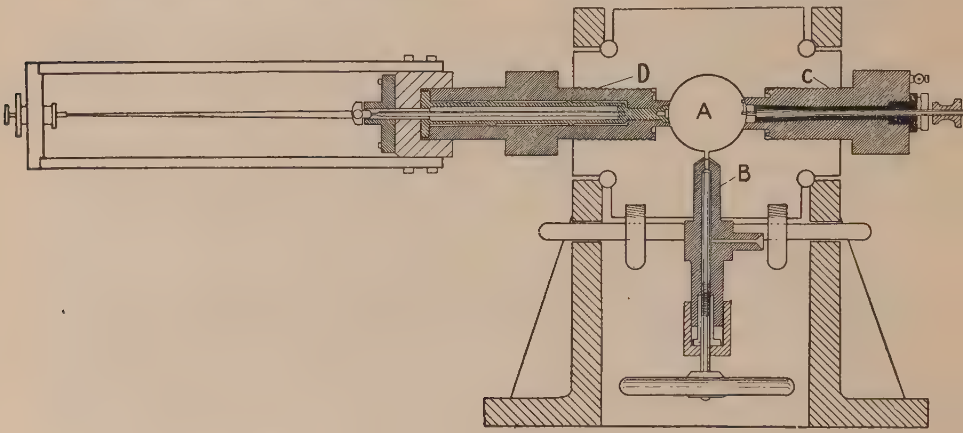

FIG. 120.—HIGH-PRESSURE EXPLOSION BOMB.

The experimental installation now includes two cylindrical and two spherical bombs capable of withstanding the aforesaid high explosion pressures, as well as two 'medium pressure' spherical bombs, the latter being capable of withstanding explosion pressures up to 100 atmospheres. One of the high pressure cylindrical bombs, capable of withstanding 1200 atmospheres pressure, is fitted at each end with quartz windows so that the explosions may be studied spectrographically. For the purpose of our present exposition, however, it will suffice to describe one of the high pressure spherical bombs, together with the Petavel manometer used in conjunction with it.

The bomb (Fig. 120) was machined out of a solid forging of open-hearth steel. Outwardly it is cylindrical in outline (10·25 in. long by 8 in.

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* *Phil. Trans.* A. 215 (1915), pp. 275 to 318; *Proc. Roy. Soc.* A. 103 (1923), p. 205; 105 (1924), p. 406; 108 (1925), p. 393; 110 (1926), p. 645; 115 (1927), p. 45.

diameter), and out of its central part has been cut a spherical cavity *A* about 3 ins. in diameter (capacity *circa* 240 c.c.). It is mounted on a cast-iron stand by means of ball bearings which permit of a rapid rotation of the bomb on its axis in order to ensure an effective mixing of its gaseous contents before an explosion. As used in an experiment the bomb is fitted with an admission valve *B*, an ignition plug *C*, and a Petavel manometer *D*. The mixtures are ignited by means of a platinum wire heated to incandescence by a direct electric current from a battery of secondary cells (12 volts), the ignition wire being situated near the wall of the explosion cavity immediately opposite the head of the Petavel manometer.

An essential part of the installation is the recording manometer of the form designed by Prof. (now Sir J. E.) Petavel in 1905 (Fig. 121), which is a most efficient appliance for high-pressure work. Perhaps the action of the gauge will be understood when it is said that, together with its optical accessories, it measures, and by a magnifying device records, the outward bulge of the walls of the explosion cavity caused by the pressure developed when the combustible mixture is fired therein, such bulge being counteracted by a very stiff spring in the head of the gauge. Now the time period θ of a vibrating system is related to W, the weight of its moving parts, and to the force A required to produce unit deflection, as follows:

$$\theta=2\pi\sqrt{\frac{W}{Ag}}.$$

In the Petavel gauge the time θ is made as short as possible consistent with the required strength (W) to withstand the sudden development of extremely high pressures, by making A, the controlling force brought into play per unit length of motion, as large as possible, in other words, by using the stiffest spring possible. By such means the time lag in registering the pressure is reduced to a minimum, which is always a most important consideration in experiments of this kind.

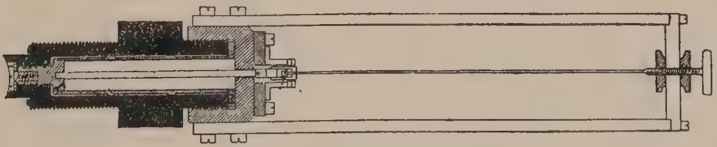

FIG. 121.—PETAVEL MANOMETER.

The spring of the gauge is tubular in shape. The actual motion produced in it by the explosion is exceedingly small, and for recording purposes it is highly magnified, first of all (*a*) by a special lever device in the gauge itself, and then (*b*) by an outside optical arrangement (Fig. 122), which focuses a point source of light upon a rapidly revolving drum, to which is attached a sensitive photographic film. The source of light is a

1000 c.p. ‘Pointolite,’ the intensity and steadiness of which enables exceedingly good pressure records to be obtained.*

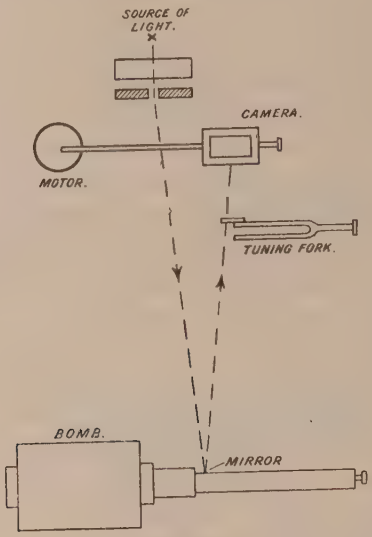

Fig. 122.

An electrically controlled tuning-fork of 100 vibrations per second is so placed that its beats interrupt momentarily the beam of light falling on the photographic film, thus recording time on the resulting pressure curve. This is subsequently calibrated by a method which need not be detailed. The intensity of this source of light and the sensitiveness of the photographic films employed up to now, have enabled us to measure quite definitely 0·005 sec. (or even less) in the pressure-time curves. A photograph of the bomb and gauge, is reproduced in Plate XXII, Fig. 123.

As an example of the kind of pressure-time records actually obtained by the foregoing means, we may give a reproduction (Plate XXII, Fig. 124) of a portion of one of our films showing the rising pressure curve obtained when a fast-burning hydrogen-air mixture was exploded in the bomb at an initial pressure of 50 atmospheres. It will be observed how quickly the pressure rose to a maximum (somewhat above 400 atmospheres), and then how the cooling period set in immediately afterwards, the time being recorded in hundredths of a second as the beam of light was momentarily interrupted by the beats of the tuning-fork. Such pressure records show

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* It may be mentioned here that the use of tubular springs lends itself very well to high pressure work where strong steel tubes are employed—but at lower pressures (say 3-10 atmospheres) much wider drawn-brass tubes have to be employed. At atmospheric initial pressure a flat or corrugated steel diaphragm (as used by Fenning) affords the best type of spring ; indeed, such a diaphragm may be used with a high degree of accuracy in explosions up to about 10 atmospheres initial pressure.

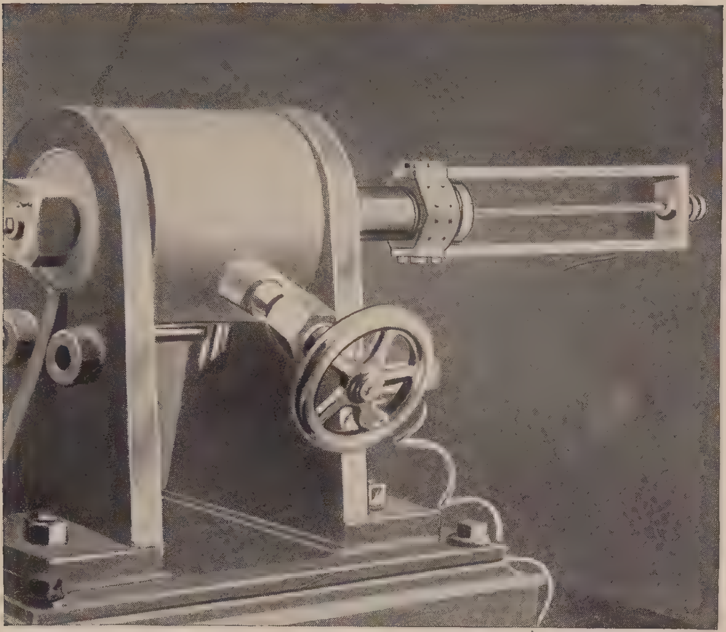

FIG. 123.—HIGH PRESSURE EXPLOSION BOMB WITH PETAVEL MANOMETER.

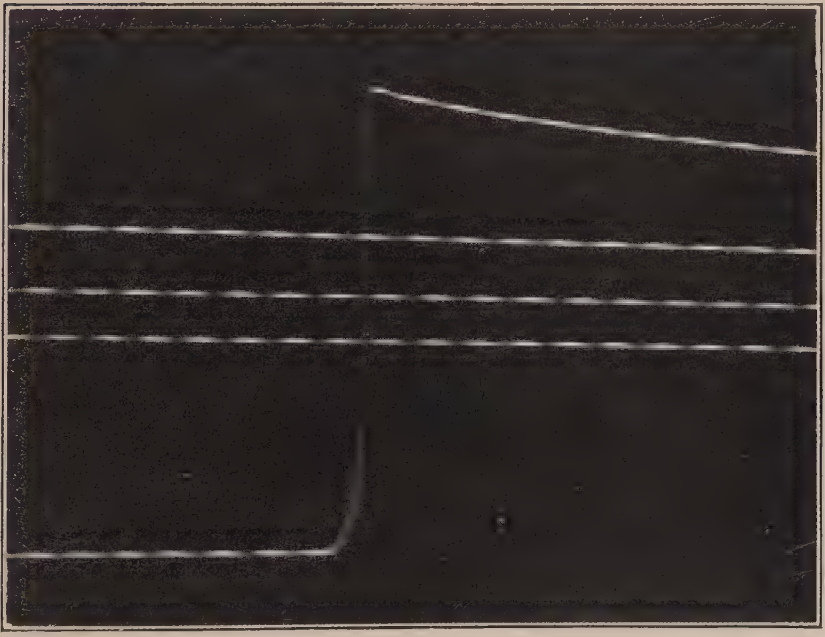

FIG. 124.—PRESSURE-TIME RECORD OF H_2-AIR EXPLOSION AT 50 ATMOSPHERES INITIAL PRESSURE.

(1) the rate at which the potential energy of the explosive mixture fired is transferred into kinetic (*i.e.* pressure or temperature) energy of the products; (2) the ratio of the maximum pressure attained on explosion to the initial pressure at which the mixture was fired—usually denoted P_m/P_i; and (3) the rate of the subsequent cooling. From a study of these and other features of the records we are able to draw conclusions as to certain fundamental aspects of the combustion process itself.

Petavel's Experiments. It should be mentioned here that Petavel had used a similar bomb in conjunction with his gauge for the investigation of solid explosives, the results of his experiments being published in 1905.*

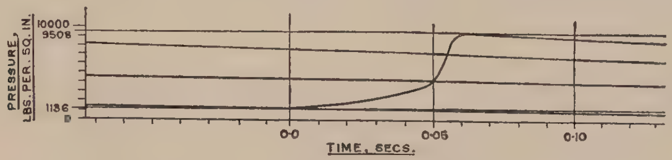

FIG. 125.—COAL-GAS-AIR EXPLOSION AT HIGH INITIAL PRESSURE. (Petavel.)
(From Clerk's *The Gas, Petrol, and Oil Engine.*)

He recorded, however, some experiments on coal gas-air explosions, and a typical time-pressure record is shewn in Fig. 125. This was obtained from the explosion of a 16·7 per cent. coal gas-air mixture fired at an initial pressure of 77·3 atmospheres in a nickel steel bomb having a spherical cavity 4 inches in diameter (capacity 552 c.c.).

The maximum pressure attained was 646 atmospheres, and hence a ratio maximum pressure/initial pressure of 8·36. From the results of other workers, Petavel considered that the corresponding ratio for the same mixture fired at atmospheric pressure would have been about 7·0 only. He attributed the higher ratio observed by him to (*a*) the departure of the gases from Boyle's Law, (*b*) the relative decrease of thermal loss during the time occupied by the combustion, and (*c*) the increase in the absolute temperature at which dissociation would take place consequent upon the higher initial pressure employed. It may be noted also how the rise to the maximum pressure shews in the middle an abrupt change of direction, a circumstance which Petavel attributed to an increased rate of pressure development when the unburnt mixture (ahead of the flame) became heated by compression to the region of its ignition temperature.

* *Phil. Trans.* A. 205 (1905), p. 357.

Researches on Hydrogen-Air and Carbonic Oxide-Air Explosions

THE CONTRAST BETWEEN CARBON MONOXIDE-AIR AND HYDROGEN-AIR PRESSURE CURVES AT AN INITIAL PRESSURE OF 50 ATMOSPHERES

We may appropriately begin by referring to the pressure-time records (Figs. 126 and 127) obtained by Bone and Haward in 1919, on exploding theoretical hydrogen-air and carbonic oxide-air mixtures, respectively, in the spherical bomb at an initial pressure of 50 atmospheres.

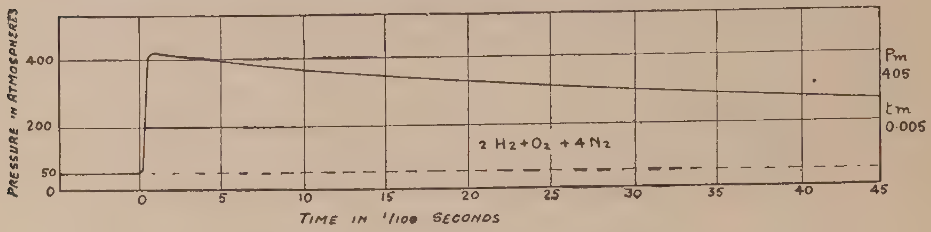

FIG. 126.—EXPLOSION OF AN H_2-AIR MIXTURE.

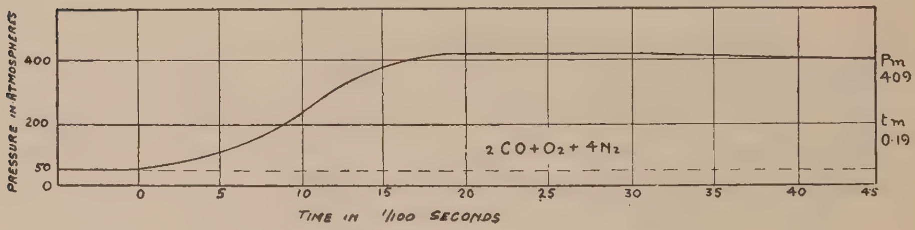

FIG. 127.—EXPLOSION OF A CO-AIR MIXTURE.

Although on explosion these two mixtures developed as nearly as may be the same total amount of energy, there was a striking contrast between the character of the pressure-time curves. For, whereas in the hydrogen-air curve the pressure rose with extreme rapidity (actually in 0·005 second) to its maximum (about 400 atmospheres), and almost immediately thereafter began to fall and assume the character of a simple cooling curve, in the corresponding carbon monoxide-air curve the pressure rose much more slowly and only attained a maximum (about 410 atmospheres) after 0·18 second, after which it was maintained almost at its maximum for a considerable time interval. The comparative slowness with which pressure energy is developed in such a carbon monoxide-air explosion, together with a considerable exothermic effect always observed after the maximum pressure had been reached, were very remarkable and significant features of the experiments. At first it was thought that this might be due to the supposed 'slow-burning' property of carbon monoxide as compared with the 'quick-burning' of hydrogen; but further experiments revealed the operation of another totally unexpected factor—namely the presence of nitrogen—which, as was discovered later, is not inert but acts as an 'energy-absorber' in the combustion of carbon monoxide at such pressures.

EFFECT OF HYDROGEN UPON THE CARBON MONOXIDE-AIR CURVE

It was next discovered that the replacement, even in very small proportions, of carbon monoxide by its equivalent of hydrogen in the theoretical carbon monoxide-air mixture had a disproportionately large influence in accelerating the rise of pressure on explosion. This remarkable result is brought out in a series of curves (Fig. 128), which demonstrate the effects of progressively replacing from one-twenty-fourth up to one-half of the carbon monoxide by its equivalent of hydrogen in the original mixture exploded. It seemed as though the hydrogen had imposed its own character upon the whole course of the carbon monoxide combustion, even when the combustible part of the mixture exploded contained only one part of hydrogen to twenty-three parts of carbon monoxide by volume.

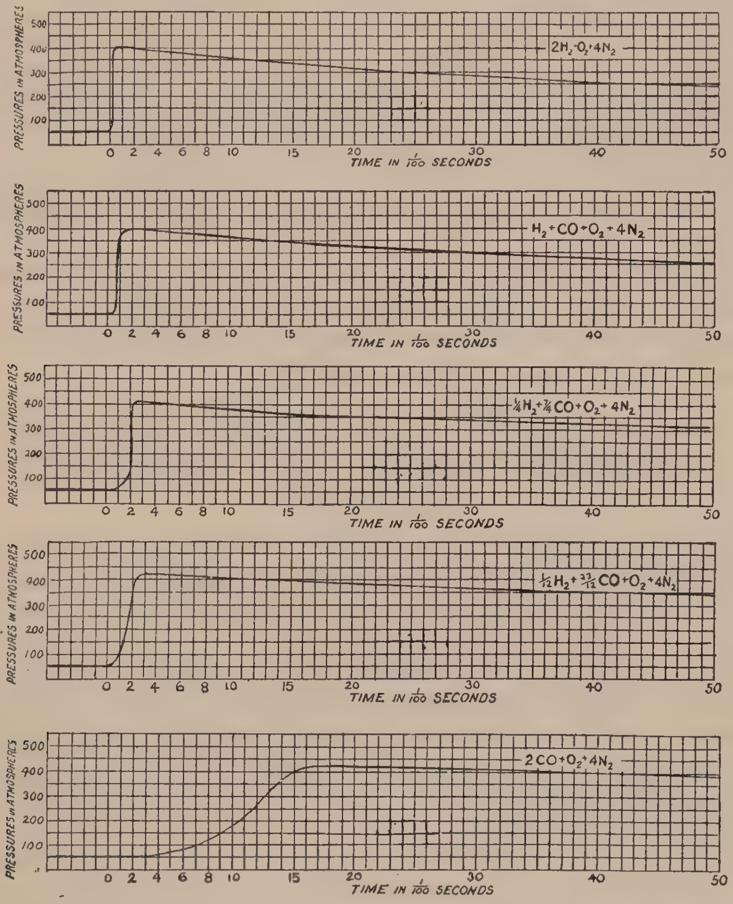

FIG. 128.—EXPLOSION OF THEORETICAL H_2-CO-AIR MIXTURES.

The results of some typical experiments are shewn below:

Approx. Composition of the Mixture Exploded.	P_i Atms.	P_m Atms.	t_m (sec.).
$2H_2 + O_2 + 4N_2$ - - -	50	400	0·005
$H_2 + CO + O_2 + 4N_2$ - -	50	399	0·015
$\frac{1}{4}H_2 + \frac{7}{4}CO + O_2 + 4N_2$ - -	50	415	0·025
$\frac{1}{12}H_2 + \frac{23}{12}CO + O_2 + 4N_2$ -	50	420	0·030
$2CO + O_2 + 4N_2$ - - -	50	420	0·180

Such results were rather puzzling at the time, and their meaning was not fully realised until after Mr. F. R. Weston's investigations on the flame spectra of hydrogen and carbonic oxide, which will be referred to in Chapter XXVI, had been completed. Nor had it then been discovered that nitrogen has a specific influence upon CO-air explosions at high pressures.

It was soon after the completion of the foregoing experiments that the accident occurred which so tragically ended poor Haward's life, and cut short a career which had given promise of great distinction in scientific research, to which he was passionately devoted.

Influence of Water Vapour on a CO-*Air Explosion at High Pressure*

Soon after the investigation was resumed in 1921, in conjunction with D. M. Newitt and D. T. A. Townend who are still associated with it, it was found that the presence of water vapour has very little influence upon the rate of pressure development in a CO-air explosion at high initial pressures. This point may be illustrated by reference to four series of experiments in which a theoretical CO-air mixture ($2CO + O_2 + 3{\cdot}77N_2$) in different hygroscopic states was exploded in the bomb at an initial pressure of 50 atmospheres. The hygroscopic condition in the system in the four series was as follows:

Series A (*Dry*). (*a*) All gases used had been previously well-dried by storage for some weeks in cylinders containing freshly distilled phosphoric anhydride, (*b*) the bomb itself and all connections had been thoroughly dried out in a current of hot air, and the explosion chamber had been kept evacuated in contact with redistilled phosphoric anhydride for three or four days immediately preceding the experiment, and (*c*) on introducing the gases into it, they were passed very slowly through a steel cylinder, 8 inches long, filled with phosphoric anhydride.

Series B (*Undried*) in which (*a*) the gases employed were directly introduced into the bomb from storage cylinders without any previous drying (*i.e.* the mixture exploded would probably contain say about 17 mm. of water vapour in 50 atmospheres, or say about 0·045 per cent.), but in (*b*) the explosion chamber had been previously dried out in a current of hot air.

Series C (*Moist*) in which the undried gases were slowly passed into the bomb from the storage cylinders through a tube packed with glass wool previously wetted with water ; they would thus carry forward into the explosion chamber more water vapour than was the case in Series B.

Series D (*Wet*). One experiment in which not only even the gases introduced into the bomb as in *C*, but also the walls of the explosion cavity had been previously wetted with distilled water.

The mean results of these experiments are shewn below:

TABLE LXXVI.—EFFECTS OF VARYING HYGROSCOPIC CONDITIONS UPON THE EXPLOSION OF $2CO+O_2+3{\cdot}77N_2$ MIXTURES AT INITIAL PRESSURE OF 50 ATMOSPHERES (BONE, NEWITT AND TOWNEND)

Series.	No. of Expts.	Hygroscopic State of System.	Pressures (Atms.).		t_m (sec.).
			Initial.	Maximum.	
A	4	Dry	50	396 to 401	0·18
B	3	Undried	50	409 to 414	0·13 to 0·15
C	3	Moist	50	390 to 398	0·18 to 0·20
D	1	Wet	50	380	0·17

It is thus seen that, so far as the time taken for the attainment of maximum pressure after the commencement of combustion (t_m) was concerned, there was little or no difference between either the 'dry' or the 'moist,' or even the 'wet' series, for in all cases it was as nearly as possible 0·18 sec. In the 'undried series,' in which the water vapour present would not exceed 1 in 2000, t_m was just appreciably shorter, namely, 0·13 to 0·15 sec. Apparently then the optimum condition for the combustion at such high pressures is reached when very little steam is present.

These results suggested strongly that at high pressures carbonic oxide and oxygen combine directly without any intervention of steam, a conclusion which was subsequently confirmed by the further experiments to be described in Chapter LXXVII, when the mechanism of CO-combustion will be fully discussed.

It thus became clear that at high initial pressures hydrogen exercises a much greater influence than does its equivalent of steam upon the rate of pressure development in explosions of theoretical CO-air mixtures.

In this connection it may be noted that in the experiments recently carried out by R. W. Fenning,* in which theoretical CO-air mixtures in various hygroscopic states were exploded at initial pressures of about 5 atmospheres, the optimum condition for combustion was reached with 2·38 per cent. only of water vapour as compared with about 6·0 per cent. for similar explosions at atmospheric pressure. It would thus appear that the amount of water vapour needed for the optimum combustion condition rapidly diminishes with the initial pressure, and at 50 atmospheres is exceedingly small. It was also found that the addition of 2·1 per cent. of a nearly dry theoretical H_2-air mixture to a dry theoretical CO-air mixture had the same effect upon the explosion curve as the addition of 1·21 per cent. of water vapour; in other words, 0·6 per cent. of hydrogen had the same effect as that of 1·21 per cent. of steam. At an initial pressure of 50 atmospheres the difference between the relative influences of equivalent proportions of hydrogen and steam on such explosions is much greater than at 5 atmospheres, for reasons probably connected with the activation of nitrogen in CO-air explosions at high pressures, a matter which will now be referred to.

Discovery of the Energy Absorbing Effect of Nitrogen in CO-*Air Explosions at High Initial Pressures*

The discovery that nitrogen exerts a peculiar energy-absorbing influence during a CO-air explosion at high initial pressures, whereby it retards the attainment of maximum pressure to a far greater degree than could be accounted for on the supposition of its acting merely as a diatomic diluent, was made in a series of experiments in which, starting with the explosion of a theoretical CO-air mixture (which for convenience of this exposition may be written as a $2CO + O_2 + 4N_2$ mixture, although air contains 3·77 of N_2 to 1·0 of O_2) at an initial pressure of 50 atmospheres, the effects of progressively replacing its nitrogen by equivalents of either oxygen, carbonic oxide or argon were studied. It was found that such replacements always progressively diminished the time required for the attainment of maximum pressure after the commencement of combustion until when the whole of the nitrogen had been so replaced the rise in pressure was nearly as rapid as in the case of a hydrogen-air mixture; moreover, the observed rate of cooling immediately after t_m was considerably accelerated by the said replacements.

Passing over the results of ' intermediate replacements ' in such a series of experiments, attention is directed to those in which the replacements were complete. The most important experimental results from this point of view are summarized in Table LXXVII, and illustrated by the set of pressure-time curves reproduced in Fig. 129.

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* *Phil. Trans.* A. 225 (1926), pp. 331 to 356.

P_i = the initial pressure in atmospheres at which each mixture is fired.

P_m = the maximum pressure in atmospheres recorded in the explosion.

t_m = the time in seconds required for the attainment of the maximum pressure after the commencement of the pressure-rise.

Σ = the thermal equivalent in K.C.U.s of the energy liberated during the explosion.

TABLE LXXVII.

Mixture Exploded.	Σ.	P_i.	t_m.	P_m.	P_m/P_i.	Per cent. Fall in Pressure in 0·5 Sec. after t_m.
$2CO+O_2+4N_2$ -	10·2	50	0·190	409	8·18	11·6
$2CO+O_2+4O_2$ -	10·0	50	0·005	460	9·20	33·33
$2CO+O_2+4CO$ -	10·4	50	0·010	450	9·00	34·3
$2CO+O_2+4Ar$ ·	10·2	50	0·025	510	10·20	26·4

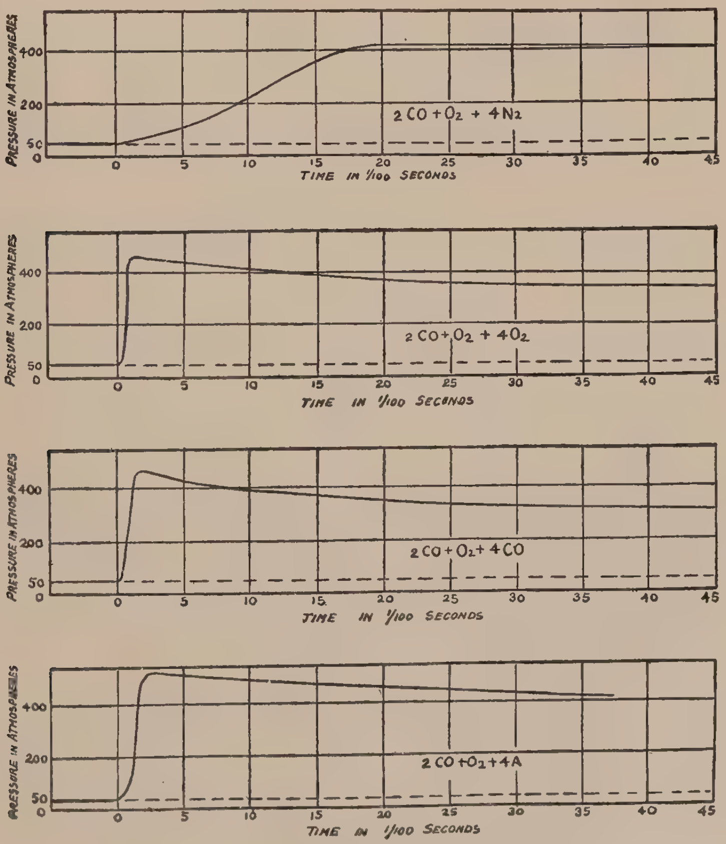

FIG. 129.—EXPLOSION OF $2CO+O_2+4R$ MIXTURES.

These and other similar results led to the conclusion that the nitrogen in the normal carbon monoxide-air mixture had been exerting a specific influence on the whole course of events, which was manifested in a threefold effect upon the pressure curves, namely:—(1) a marked retardation of the rate of attainment of maximum pressure, (2) a lowering of the observed maximum pressure, and (3) a considerable retardation of the subsequent cooling due to a peculiar exothermic effect produced by the nitrogen. For whenever such nitrogen was wholly replaced by its molecular equivalent of any one of the other three gases the development of pressure became nearly as rapid as in the explosion of a normal hydrogen-air mixture under like conditions. Moreover, comparative analyses of the pressure-time records obtained during the experiments in question have shewn that, when nitrogen was present, much less kinetic (pressure) energy was absorbed up to the attainment of maximum pressure than was subsequently liberated as the said exothermic effect during the cooling period. This remarkable circumstance indicated that a considerable part of the radiation emitted by the burning carbon monoxide (which otherwise would have been absorbed by the walls of the explosion vessel) had been intercepted by the nitrogen present and was subsequently degraded and liberated as sensible heat during the cooling period.

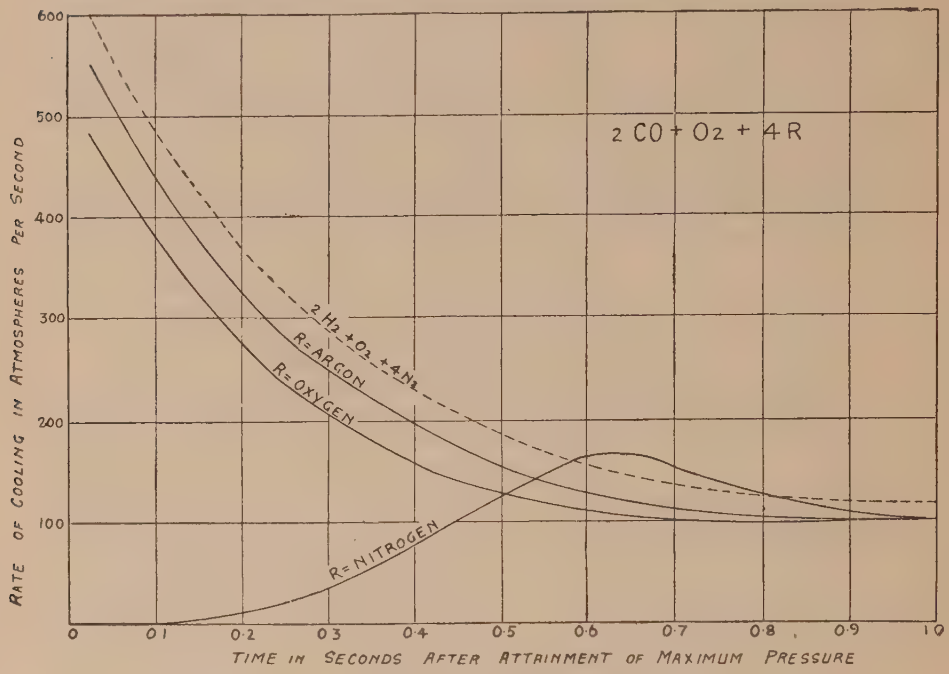

FIG. 130.

The following graphs (Fig. 130) shew the rates of cooling (expressed as pressure fall in atmospheres per second) of the gaseous systems immediately after the attainment of maximum pressure, when each of the four mixtures

$$2CO + O_2 + 4N_2,\ 2CO + O_2 + 4O_2,\ 2CO + O_2 + 4Ar, \text{ and } 2H_2 + O_2 + 4N_2,$$

respectively, was exploded in the bomb at an initial pressure of 50 atmospheres. It will be seen that, except in the case of the carbon monoxide-air mixture, the cooling was perfectly regular, and presented no abnormal features whatever. In the case of the $2CO + O_2 + 4N_2$ mixture, however, there was no cooling at all during the 0·1 sec. after the attainment of the maximum pressure, and it was not until the lapse of 0·6 sec. thereafter that anything like a normal rate of cooling was established. Attention is specially directed to the striking contrast between the perfect normality of the first 0·6 sec. of the cooling period in the case of the hydrogen-air ($2H_2 + O_2 \ + 4N_2$) mixture, and its complete abnormality in the case of the corresponding carbon monoxide-air mixture. This circumstance, combined with the perfect normality of the cooling in the case of the $2CO + O_2 + 4Ar$ mixture, can hardly be explained except on the assumption that the nitrogen functions differently in a hydrogen-air explosion, where it acts as an inert diluent only, from what it does in a carbon monoxide-air explosion, where, in addition to its ordinary diluent action, it has a peculiar ‘energy absorbing’ effect and becomes chemically ‘activated.’ On such an assumption the meaning of the $2CO + O_2 + 4N_2$ cooling curve is that the radiant energy which had been absorbed by the N_2 molecules during the previous combustion period was being slowly evolved in a kinetic form far into the subsequent cooling period, the ‘activated’ nitrogen not having entirely reverted to normal until at least 0·6 sec. after the end of the combustion period.

In further experiments explosions of the foregoing mixtures have been carried out over a very wide range of initial pressures,* namely, from 3 up to 175 atmospheres, with striking confirmation of the views already discussed. For, if as was supposed, nitrogen intercepts and absorbs the radiation emitted by burning carbonic oxide, it might be anticipated that the phenomenon would be influenced considerably by the degree of initial compression under which the mixture was exploded. For the greater density of the nitrogen in the explosion chamber the greater would be the chance of its intercepting the radiation in question. Indeed it might be expected that there would be some limiting compression below which the phenomenon would hardly be discernible, and the more the initial compression was increased above such limit the greater would be the resulting effect.

The following figures shew how completely such expectation was fulfilled, for it was found that only in the case of explosions of a carbonic oxide-air mixture did progressive increase in the initial pressure result in a progressive retardation in the pressure development; in all other cases the explosion tended to become quicker as the initial pressure increased.

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* *Proc. Roy. Soc.* A. 105 (1924), p. 406 ; *ibid.* 108 (1925), p. 393.

TABLE LXXVIII.—INFLUENCE OF INITIAL PRESSURE ON THE TIMES TAKEN FOR THE ATTAINMENT OF MAXIMUM PRESSURE (BONE, NEWITT AND TOWNEND)

Mixture.	Initial Pressure (Atmospheres).									
	3	25	50	75	100	125	150	175		
$2CO+O_2+4N_2$	0·07	0·15	0·19	0·32	0·40	0·47	0·53	0·56	sec.	t_m
$2CO+O_2+4O_2$	0·06	0·01	0·005	0·005	—	—	—	—	,,	
$2CO+O_2+4CO$	0·035	—	0·010	0·01	0·005	0·005	0·005	—	,,	
$2CO+O_2+4Ar$	0·035	—	0·025	0·015	0·010	0·010	0·010	—	,,	
$2H_2+O_2+4N_2$	In all cases ·005 second (or less), tending to become smaller as the initial pressure was raised.									

It is important to observe that with an initial pressure as low as 3 atmospheres not only were the rates of pressure development in cases of a $2CO+O_2+4N_2$ and $2CO+O_2+4O_2$ mixtures nearly the same, but the pressure-time curves as a whole were almost identical; indeed, they could almost be superposed on each other. This circumstance shews that no appreciable N_2-activation had occurred at such a low pressure; indeed it did not become manifest until the initial pressure was raised to 10 atmospheres, after which it increased with the initial pressure until at 25 atmospheres upwards it became very marked.

It is desirable to stress certain points here, namely: (1) that the 'energy absorbing' nitrogen effect referred to was only obtained when carbon monoxide and oxygen were in juxtaposition in such high pressure explosions, as though it were essentially a 'resonance' effect, (2) that the presence of hydrogen, which (as will be seen later) profoundly affects the radiation for a CO-air explosion, is inimical to it, a circumstance pointing to the 'effective radiation' being that arising from $CO\text{-}O_2$, but not from $CO\text{-}OH_2$ interactions, (3) that pressure is highly conducive to it, and (4) that recent experiments have shewn that it is not manifested in methane-air $(CH_4+O_2+4N_2)$ explosions at high pressure, where equal volumes of carbonic oxide, hydrogen and steam are produced.

Secondary NO-*Formation in* CO-*Air Explosions*

Another striking feature of CO-air explosions at high initial pressure is that, provided oxygen be present in excess of that required to burn all the carbonic oxide, large quantities of nitric oxide are produced. Such NO-formation is, however, a *secondary* effect, usually occurring during the cooling period, *i.e.* after the attainment of maximum pressure, though with increasing initial pressure it may begin sooner. The amounts of it produced far exceed those predicted for a purely thermal equilibrium in an NO-air system at the maximum explosion temperature. Thus, for example, in one experiment in which a mixture of 2 volumes of carbonic oxide and 6½ volumes of air was exploded in a large cylindrical bomb at an initial pressure of 25 atmospheres, the maximum temperature being no higher than 2120° Abs. (attained in 0·45 sec.), the cooled products contained 2·8 per cent. of nitrogen peroxide, whereas, according to Nernst, the proportion of NO in thermal equilibrium with air at such temperatures would only be 0·8 per cent.*

Nitrogen Activation in CO-*Air Explosions*

Consideration of space precludes our discussing further the mass of cumulative evidence—including some recent spectrographic results—forthcoming during the research in regard to the energy-absorbing effect of nitrogen, and the secondary NO-formation in CO-air explosions at high initial pressures. It is all set forth in the published papers (*q.v.*), and will be dealt with fully in the supplementary volume which we hope shortly to publish on gaseous combustion at high pressures. In the meantime, the principal facts, and our explanation of them, may be summarised in the following paragraphs.

The outstanding facts in regard to the explosions of CO-air mixtures are that (1), *contrary to all other cases yet examined*, progressive increases in the initial pressure between 3 and 175 atmospheres cause progressively longer 'time-lags' in the attainment of maximum pressure when a theoretical mixture is exploded in a bomb, (2) as soon as such time-lag becomes manifest, and for a considerable range of initial pressures thereafter (3 to nearly 25 atmospheres), it is always characterised by a marked exothermic effect during the 'cooling period,' without any appreciable lowering of the 'corrected' maximum pressure, as compared with that for a $2CO+O_2+4CO$ or $2CO+O_2+4O_2$ mixture, (3) such effects are observed only when CO and N_2 are in juxtaposition in an explosion and are rapidly counteracted when hydrogen is gradually added to the explosive mixture, (4) when more oxygen is present than is required to burn all the carbonic oxide a secondary NO-formation occurs, which is favourably influenced by increasing pressure and at high initial pressure far exceeds that corresponding with a merely thermal equilibrium in a NO-air system at the maximum explosion temperature, (5) spectrographic investigations have shewn that at initial pressure up to at any rate 25 atmospheres (or as far as such experiments have been carried), and probably higher, the said NO-formation does not begin during the 'combustion' period or until *after* all the resulting ultra-violet and visual radiation capable of affecting a sensitive photographic plate has been emitted, and (6) in such explosions any excess of CO or N_2 present as a diluent strongly absorbs the ultra-violet radiation emitted by a $2CO + O_2$ explosion, such absorption being general, though not uniform, over the range A.U. 4400 to 3200.

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* *Zeit. Anorg. Chem.* 45 (1905), 110; 49 (1906), 212, 229.

These facts are all explained on the suppositions (1) that the radiation emitted in a CO-oxygen explosion at high pressure is absorbed by the combustible gas, which is thereby 'activated' so as to be capable of combining directly with oxygen, (2) that when nitrogen is present as a diluent, as in a CO-air explosion, part of the radiation so emitted is intercepted and absorbed by the nitrogen (which is thereby 'activated'), so that the rate of activation of the CO molecules is retarded, thus producing the observed 'lags' in the attainment of maximum pressure, which 'lags' increase with the density of the medium, and (3) the nitrogen so 'activated' either (*a*) reverts to the ordinary state during the 'cooling period' liberating (as sensible heat) the equivalent of the radiant energy which it absorbed during the 'explosion period,' or (*b*) where excess of oxygen is present, combines with it forming nitric oxide.

It should be understood that by the term 'activated nitrogen' the highly ionised 'active nitrogen' discovered by the present Lord Rayleigh is not implied, but a less 'activated' form; also, that the radiation concerned, though it may in part be ultra-violet, is more probably infra-red, a point which has yet to be decided experimentally. All such matters will, however, be dealt with in our supplementary volume.

Some Other Features of High Pressure Explosions

Perhaps one of the most striking observations made in the study of gaseous explosions at high pressures is the large increase in the ratio of maximum to initial pressure (P_m/P_i) which occurs as the initial pressure is raised. Such ratios for four standard mixtures are given in the following Table. It should be observed that all the maximum pressures have been corrected for any cooling loss which may occur during the time taken for attainment of maximum pressure, and the initial pressures for any deviation from Boyle's law.

TABLE LXXIX.—RISE OF P_m/P_i RATIOS WITH INCREASING INITIAL PRESSURE (BONE, NEWITT AND TOWNEND)

Mixture.	Corrected P_m/P_i Ratios.			Percentage Increase in P_m/P_1 Ratio.	
	$P_i = 3$ Atms.	$P_i = 75$ Atms.	$P_i = 150$ Atms.	3 to 75 Atms.	3 to 150 Atms.
$2H_2 + O_2 + 4N_2$ -	7·7	8·43	8·82	9·5	14·3
$2CO + O_2 + 4CO$	8·0	9·48	10·16	18·5	27·0
$2CO + O_2 + 4N_2$	7·8	9·14	9·76	17·2	25·3
$2CO + O_2 + 4Ar$	8·65	10·30	11·20	19·0	29·5

It should be observed that (1) the increase in the case of the H_2-air mixture was at about half the rate observed in the other cases, and (2) in all cases the increase between 3 and 75 atmospheres was about two-thirds that over the total range of 3 to 150 atmospheres. The remarkable constancy of the observed effect suggests its connection with some fundamental physical feature of the experiments, though it has been shewn to be independent of dissociation effects, cooling loss, or deviation of the initial mixture from Boyle's Law. Various suggestions have been advanced, but the matter is too complex for discussion in this chapter; it will be referred to in our proposed supplementary volume.

Lastly, it is of interest to note how high pressure may effect the relative influences of 'conduction' and 'radiation' factors upon the cooling after the attainment of maximum pressure. Thus in the following table are shewn the mean rates of cooling, expressed as powers of T abs., during successive half-seconds after the attainment of maximum pressure in the case of the two mixtures $2H_2 + O_2 + 4N_2$ and $2CO + O_2 + 4CO$.

TABLE LXXX.—MEAN RATES OF COOLING IN SUCCESSIVE HALF-SECONDS IN POWERS OF T ABS. (BONE, NEWITT AND TOWNEND)

Initial Pressure (Atms.).	10.		50.		100.		150.	
First (1) and second (2) half-second intervals after P_m.	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
(1) $2H_2 + O_2 + 4N_2$ -	1·9	1·9	1·8	1·8	1·9	1·9	1·8	1·8
(2) $2CO + O_2 + 4CO$ -	2·0	2·0	3·0	2·8	3·4	2·8	4·0	2·6

These figures indicate that the relative influence of 'radiation' in the carbonic oxide explosions (as distinct from the hydrogen explosions) increased progressively with the initial pressure, a circumstance which shews that in such explosions at high initial pressures, nitrogen being absent, the products are in a highly radiative condition at, and during a measurable time interval after, the attainment of maximum pressure. They also suggest that at high pressures the excess of carbon monoxide in (2) was capable of absorbing, and retaining for a brief time interval after t_m, some of the radiation emitted during the actual combustion period.

CHAPTER XXIII

THE PROBLEM OF 'KNOCK' IN PETROL-AIR ENGINES

Although it is outside the ambit of our purpose to deal with the special problems of internal-combustion engines, the question of 'knock' in connection with vapour-air explosions, which is fundamentally a chemical one, has come so much to the front lately that some reference to it here will not be out of place. And, in order that its importance may be understood by chemists, it is necessary to preface our treatment of it by a few words about some recent work relating to the influence of compression upon thermal efficiencies attainable in such engines.

Whereas our knowledge of gaseous explosions mostly relates to flame propagation through more or less stagnant media at atmospheric temperature and pressure, modern high-speed engines are capable of performing up to 2500 (or even more) revolutions per minute, and under such conditions combustion must proceed with great rapidity in an explosive medium which is (1) under compression, (2) raised to a temperature of a few hundred degrees, and (3) in a highly turbulent state. It is, therefore, reasonable to suppose that in such circumstances factors may be operative which are not observable under ordinary conditions.

It is of great importance to designers of internal-combustion engines to be able to determine accurately the thermal efficiency of any particular engine working under standard conditions. Whilst it would be out of place here to deal with the thermodynamical consideration of this problem it may be said that in practice the observed thermal efficiency of an engine (determined by experimental test) is generally compared with that which would obtain if the working fluid (gaseous medium) were 'ideal air,' *i.e.* a perfect gas whose specific heat is constant at all temperatures and the ratio of whose specific heats at constant pressure and volume respectively is 1·4, adiabatic conditions being assumed. Such a standard, though forming a suitable basis of comparison, is far removed from that attainable in practice, because heat loss is always an important factor, and the physical properties of the gaseous mixtures concerned are never the same as those of 'ideal air.'

The main difficulty experienced in considering such experimentally determined values is that of forming an accurate estimate of the efficiency, compared with the 'ideal air' standard, which might reasonably be expected from a knowledge of the heat of combustion and other thermal properties of the particular explosive mixture employed. In the case of engines working on liquid fuel, this question formed the subject of an exhaustive enquiry in 1921 by Tizard and Pye who examined it in the light of Pier and Bjerrum's results (see previous chapter) in regard to (*a*) the molecular heat capacities, and (*b*) the dissociation constants of steam and carbon dioxide at high temperatures. The results of this new enquiry shewed (*a*) the importance of the part played by dissociation in reducing thermal efficiency, and (*b*) that, when dissociation had been allowed for, the calculated efficiency in any particular case was in remarkable agreement with that observed in actual test. Thus, it was found that under their experimental conditions the effect of dissociation on the thermal efficiency for a 'theoretical' mixture of vapour and air was to lower it by 6 per cent. Moreover, the maximum power attained in an explosion was not generated with the 'theoretical' mixture, but with mixtures containing a definite excess of combustible vapour. The thermal efficiency was also found to be very much greater when a weak mixture was employed, the explosion temperature in such circumstances being much lower with consequent reduction of dissociation and mean molecular heat capacity.

With a weak mixture at a compression ratio of 5 : 1, an efficiency (based on the 'ideal air' standard) of 38 per cent. was calculated, which compared with an observed efficiency of about 32 per cent. And, seeing that the difference corresponded with the estimated heat loss, the agreement was considered satisfactory. From this the conclusion was drawn that there was little chance of improvement in design bringing about a substantial increase in the thermal efficiency of an engine operating at a definite compression ratio. According to Tizard, however, even greater indicated thermal efficiencies have been recorded recently than would seem possible from calculations based on Bjerrum's dissociation and specific heat data, and he has expressed the opinion that these values need revision.*

Influence of Compression Ratio on Thermal Efficiency

It has long been known that the theoretical efficiency of an engine calculated on the usual thermodynamical formula : $E=1-\left(\frac{1}{r}\right)^{\gamma-1}$, (where r=the compression ratio and γ the ratio of the specific heats at constant pressure and volume, respectively), shews a considerable increase as the compression ratio is raised, 'ideal air' being the standard.

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* *Trans. Faraday Soc.* (1926), p. 352.

Tizard and Pye, however, shewed that when values for γ calculated according to the composition of the mixture and the degree of dissociation estimated were applied, even greater increases in efficiency might be expected.* This was of great interest, seeing that it has been doubted in some quarters whether even the increase calculated on the 'ideal air' standard could be attained in practice.

Accordingly, tests were carried out in a Ricardo variable-compression engine with a theoretical vapour-air mixture with results as shewn in the following table :

Table LXXXI.—Influence of Compression Ratio on Thermal Efficiency (Tizard and Pye)

Compression Ratio.	Maximum Thermal Efficiency.		Ratio $\frac{\text{Observed}}{\text{Calculated.}}$
	Calculated.	Observed.	
4 to 1	0·337	0·277	0·82
5 to 1	0·380	0·316	0·83
7 to 1	0·440	0·372	0·85

It is thus clear that the predicted rise of relative thermal efficiency was fully confirmed by the subsequent experimental tests.

It seems to be generally accepted amongst engineers that the compression ratio in modern engines could be increased without placing undue strain on mechanical parts. Unfortunately, however, such increase is very limited in practice owing to the occurrence of the phenomenon known as 'knock.' In this connection Tizard has recently said, "anyone discovering a practical method of so controlling the rate of combustion of fuels as to enable the average expansion ratio of petrol engines to be raised from, say 5 : 1 to 7 : 1—an alteration which involves little or no engineering difficulties—would save the country in time several million pounds a year. There is probably no subject which combines more practical and scientific interest at the present time; the researches of the last few years have taught us how little we know of the nature of gaseous reactions at very high temperatures, in spite of all the work of the past."

'Knock' in Engines

Under certain conditions of running, particularly when high compression ratios are employed, explosions in motor-engines may not recur smoothly but the phenomenon of 'knock' may be encountered with consequent loss of efficiency and strain on the working parts. In such circumstances a fugitive and abnormally high pressure, accompanied by a sharp metallic ring, is developed instantaneously, the cylinder walls receiving as it were a 'hammer blow' instead of an effective thrust; indeed the circumstances associated with the phenomenon simulate those of detonation.

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* *Rep. Empire Motor Fuels Committee*, Inst. Auto. Eng. (1923).

This aspect of the subject was studied by H. B. Dixon in 1920, who found, however, that it was exceedingly difficult in his long tube apparatus to set up a detonation wave in a vapour-air mixture, and only in the cases of alcohol and ether could it be propagated at all, although when the air was replaced by oxygen the mixtures could be made to detonate without difficulty.*

Moreover, the possibility of the setting up of a detonation wave in such a motor-engine has been questioned on the ground that the size of the cylinder does not allow of a flame travelling the necessary distance for its formation (see Chapter LXVI). Against this it may be pointed out that both Laffitte † and Egerton and Gates ‡ have shewn that under the influence of pressure detonation waves may be established in much shorter distances than are necessary at atmospheric pressure, and generally speaking it should be remembered that the conditions prevailing in an engine are far removed from those at which any detailed study of the setting up of detonation waves can be made experimentally.

There are other reasons, however, for doubting whether a true detonation wave can be established in the engine cylinder. It has been shewn in Chapter XV, how the setting up of a detonation wave in a closed tube is largely influenced by the repeated effects of reflected compression waves. These largely depend on the symmetry of the containing vessel, and ordinary engine cylinders are very irregular in shape. Also, it has been thought by some that, owing to the turbulence of the explosive mixtures concerned, there is less likelihood of the continued propagation of high compression waves or of any form of violent oscillation. On this account modern theories tend towards the idea that 'knock' is due to the spontaneous ignition of the unburnt charge which has been compressed above its ignition point by the expansion of the already combined gases.

Tizard has drawn attention to the fact that the tendency of fuels to 'knock' is closely connected with their ignition temperatures. Thus the ignition temperatures of the paraffin hydrocarbons diminish steadily as their molecular weight increases, and it has been found that the higher members of the series give rise to 'knock' more easily than the lower ones. The fact that benzols are less liable to it than the corresponding paraffins (*e.g.* benzene than hexane) suggests that chemical structure also plays a part. Another interesting fact observed by Tizard and Pye is that in certain cases the tendency to 'knock' is related to the rate of pressure development observed when certain explosive mixtures are compressed adiabatically to temperatures well above their ignition temperatures. Thus, whereas the ignition temperature of carbon disulphide is lower than that of heptane, the latter gives rise to 'knock' in an engine more easily; and when corresponding mixtures are compressed adiabatically to temperatures above their respective ignition points, the development of pressure is far more rapid when heptane is used as the combustible.

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* *Report of the Imperial Motor Transport Conference* (1920).

† *Comptes rendus* 183 (1926), p. 284.

‡ *Proc. Roy. Soc.* A. 114 (1927), p. 137.

In the general case it seems agreed that any factor which will help to reduce the temperature attained, either locally or generally, in the unburnt explosive medium will also reduce the tendency to 'knock.' Thus the greater the turbulence of the mixture the less tendency will it have to 'knock'; moreover, addition of a proportion of the exhaust gases, or of excess air, to the mixture will have the same effect. 'Knock' is also more prevalent when heat conduction is poor, such as when a cylinder becomes carbonised, or when its proportions are too large. The presence of constricted spaces or pockets where heat may accumulate should also be avoided.

On the effect of pressure opinion seems to vary. It may be argued, on the one hand, that the indirect effect of increased compression-ratio is merely one of raising the explosion temperature by influencing cooling losses and dissociation. On the other hand, it has been claimed that the effect of pressure is a direct one.

Although results observed in explosions in ordinary bombs are not very comparable with those occurring in motor-engines, the experiments of Fenning on the subject carried out at the National Physical Laboratory—with the apparatus described in the last chapter—are of interest.

He made a study of the influence of varying initial temperatures between 100 and 300° and of initial pressures from about 37 to 146 lbs. per sq. inch on the explosion of various mixtures of benzene, hexane, and petrol with air.* First of all a series of experiments was carried out at an initial temperature of 100° C. and a pressure of 93 lbs. per sq. inch in order to study the effect of varying the mixture-strength in such cases. It was found that in the case of all three fuels *rich* mixtures gave rise to 'knock,' the intensity of which varied inversely as the air to fuel ratio, and the 'knock' appeared to be preceded by high frequency vibrations.

The pressure-time curves shewn in Plate XXIII illustrate the effects found with air-petrol mixtures whose air/fuel weight-ratio varied from 19·2 to 8·9. The two lowest records shew very well the violence associated with the pressure rise when 'knock' occurs.

It was also found that whereas on raising the initial temperature to 300° C. the 'knock' was suppressed in the case of rich benzene-air mixtures, in the case of rich hexane- or petrol-air mixtures it still persisted.

In the case of the 'theoretical' mixtures of all three fuels the explosion-time diminished as the initial temperature was raised but increased with

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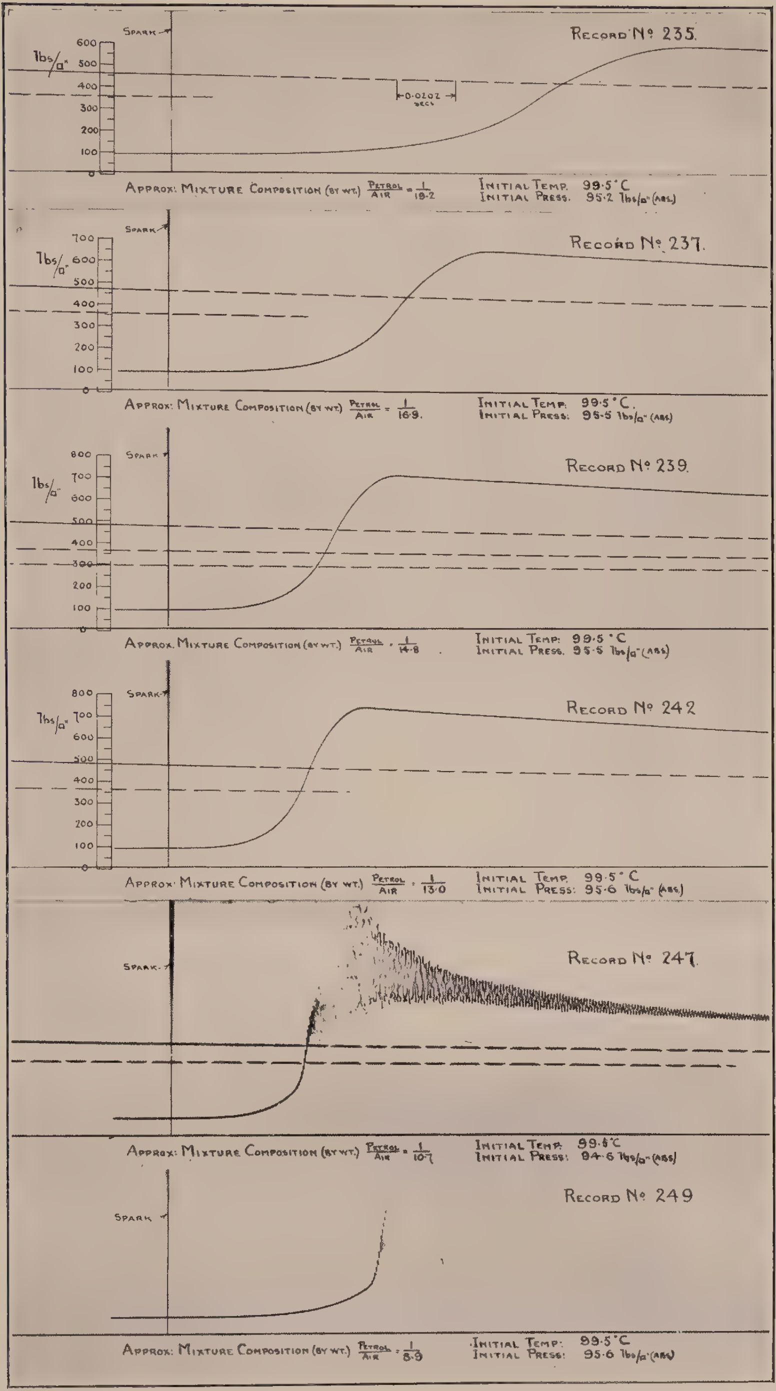
* *Rep. and Mem. Aeronautical Research Committee, No.* 979 (1925).

PLATE XXIII.



Pressure-Time Records of Petrol-Air Explosions. (Fenning.)
(From *Rep. and Mem. Aeronautical Research Committee.*)

the initial pressure, the rate of increase with pressure diminishing at higher initial temperatures. Raising the initial temperature of the theoretical air-petrol and air-hexane mixtures led to ‘ knock ’ of increasing intensity, the defect first appearing at higher initial pressures and extending to lower ones as the initial temperature increased. With the theoretical air-benzene mixture, however, there was no such indication of the production of ‘ knock ’ with increase of initial temperature.

An interesting feature of Fenning’s curves is the fact that in all cases ‘knock’ ensued after the chemical combination had progressed normally for some time and that its violence varied with the amount of normal combustion which had already taken place. Moreover, at any one initial temperature the amount of ‘ pre-knock ’ combustion became slightly less as the initial pressure was raised.

Anti-Knocks

The tendency to ‘ knock ’ is not a marked property of all fuels. The members of the paraffin series and ether are among the worst offenders, but aromatic hydrocarbons or alcohol are comparatively free from the defect under ordinary conditions. Indeed, the marked tendency of petrol fuels to ‘ knock ’ may be diminished or suppressed by diluting them with benzol. The standard test now generally recognised for classifying fuels according to their tendency to ‘ knock ’ is that of the “ Highest Useful Compression-Ratio ” (H.U.C.R.), which has been defined as “ the compression at which detonation first becomes audible with certain definite temperature conditions and with both the ignition and mixture strength adjusted to give the highest efficiency. It is not the highest compression which can be employed, but the highest that it is worth while to employ.” The addition of toluene to petrol definitely raises its H.U.C.R. proportionately to the amount added.

In 1922 Midgley * announced the important discovery of ‘ anti-knocks,’ or substances which, when added to liquid fuels in very small proportions, have the effect of suppressing their tendency to ‘ knock.’ The figures in Table LXXXII., p. 296, shew the proportions by volume of some such substances which when added to a fuel had the same effect as 25 per cent. of benzene.

The ‘ knock ’ suppressing characteristics were ascribed to the particular metallic or other atom † present which on thermal decomposition of the ‘ anti-knock ’ reduced the velocity of combustion. It was thought that the effect might be brought about by such atoms acting as screens in selectively absorbing radiation and thereby reducing flame velocity.

The list of substances acting as ‘ anti-knocks ’ mainly comprises organo-metallic compounds, metallic carbonyls and other purely organic compounds (*e.g.* dimethyl aniline), and it has been considerably extended

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* *J. Ind. Eng. Chem.* (1922), p. 589.

† Iodine or Nitrogen for example.

Table LXXXII.—Relative Effects of some ‘ Anti-Knock ’ Compounds (Midgley)

Compound.	Corresponding Per Cent. by Volume.	Corresponding Number of Molecules of Theoretical Air/Fuel Mixture to One Molecule of Anti-Knock.
Benzene	25	150
Ethyl Iodide	1·6	2,150
Xylidine	2·0	2,600
Tin Tetra-ethyl	1·2	7,100
Di-ethyl Selenide	0·4	11,750
Di-ethyl Telluride	0·1	50,000
Lead tetra-ethyl	0·04	215,000

during the last few years. The supposition that the action of organometallic compounds is due to the metallic atoms present has been confirmed recently in an ingenious way by Sims and Mardles,* who shewed that an equally good, or even better, effect may be obtained merely by adding a ‘ metallic-sol ’ (*i.e.* a colloidal solution of the metal in petrol) to the fuel, as the following figures shew :

Metal Present.		Increase in H.U.C.R. (Per Cent.).
Nickel	Nickel Sol † in B.P. petrol	41·5
	Nickel Carbonyl	38·0
Lead	Lead Sol † in B.P. petrol	33·8
	Lead Tetra-ethyl	35·0
Iron	Iron Sol † in B.P. petrol	45·4
	Iron Carbonyl	41·0

Since Midgley’s discovery, the action of ‘ anti-knocks ’ has naturally given rise to much speculation. Obviously their effect cannot be explained on purely thermal grounds, for they are never present in sufficient quantity to have any appreciable influence in lowering the temperature of the reaction. Moreover, it has been shewn that their presence has little influence on ‘ flame velocities,’ or the setting up of detonation waves.

Considerable discussion has centred round the question as to whether or not ‘ anti-knocks ’ interfere in any way with the degree of ionisation occurring in explosions. Thus Wendt and Grimm ‡ put forward the hypothesis that the observed effect was one of diminishing the degree of ionisation. In support of this they shewed that on passing air ionised in an electric arc over benzene either (*a*) pure or (*b*) containing ‘ anti-knocks ’ and thence into an electroscope, the medium was more highly charged in

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* *Rep. amd Mem. Aeronautical Research Committee, No.* 1021 (1926).

† For the various methods of preparing these sols the original paper should be consulted.

‡ *J. Ind. Eng. Chem.* 16 (1924), p. 890.

(*a*) than in (*b*), thus indicating a specific influence on the part of the 'anti-knock' in accelerating the recombination of the ions. On the other hand Clerk, Brugmann and Thee,* using X-rays instead of an arc as a source of ionisation, failed to confirm such results.

The experiments of Malinowsky † in this connection are also of interest. He claimed to have arrested the explosion wave in a benzene-air mixture by passing it through metal plates having a potential difference of a few hundred volts, although he was unsuccessful in so doing in the case of other gaseous explosive mixtures. Moreover, when electrons were removed from the explosion wave in this way the flame travelled some distance before normal conditions were restored. In view, however, of the negative results of Dixon ‡ and Lind § in this connection, the subject seems to need much further exploration.

Another suggestion has been made by American investigators (Taylor, Charch, Mack and Boord) that the action of lead-ethyl in suppressing 'knock' is associated with the liberation of fine particles of the free metal in the gaseous mixture, which, functioning as catalysts, and themselves undergoing rapid oxidation, produce at a definite stage of the engine cycle a large number of oxidation centres. Not only may metallic atoms function as oxidation centres, but also free radicals, *e.g.* C_2H_5, liberated by thermal decomposition of organo-metallic or organic 'anti-knock' substances. In this way a homogeneous combustion throughout the gas mixture ahead of the flame front might occur, thereby suppressing 'knock.' ¶

Recently H. L. Callendar || has made some new suggestions concerning 'knock' in engines. He points out that vaporised hydrocarbons, and particularly those of high molecular weight, will tend to condense on adiabatic compression and to form minute liquid drops ('nuclear drops'), an effect which would be the reverse in the case of steam. Particularly would this be the case when the fuel is injected as a spray, or when carbon particles are present, thus supplying nuclei for the initiation of condensation. Moreover, the greater the compression ratio, the greater would be the tendency of the fuel to condense. In the case of petrol, for example, such drops would consist of the heavier molecules having the lowest ignition temperatures. Being freshly condensed, they would also be in an active state, and on absorbing oxygen will become *loci* of chemical reaction and ultimately give rise to spontaneous ignition throughout the mass. The effectiveness of 'anti-knocks' is thus explained on the supposition that they naturally become concentrated in such molecular drops, where they would decompose depositing metal and thereby delaying the oxidation of the drops. The action of organic 'anti-knocks' is assumed to be one

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* *J. Ind. Eng. Chem.* 17 (1925), p. 1226.

† *J. Chim. Phys.* 21 (1924), p. 469.

‡ See Chapter xvi, p. 186.

§ *J. Phys. Chem.* 38 (1924), p. 57.

¶ *Nature* 119 (1927), 746.

|| *Rep. and Mem. Aeronautical Research Committee, No.* 1013 (1926).

of diluting the 'nuclear drops' whereby their ignition temperature is raised. It is assumed that such 'nuclear drops' represent a very small proportion only of the total hydrocarbon fuel present, thus explaining why only very small additions of the 'anti-knock' substances are required to suppress 'knock' altogether.

Tizard has pointed out that this hypothesis is open to the criticism that the hydrocarbon vapour is so far from being saturated at the compression temperature reached that the possibility of liquid drops being formed is hardly admissible, and further that in the majority of cases the compression temperature is actually higher than the critical temperatures of the hydrocarbons concerned. Also, whilst it is possible that some such condensation may occur in the case of the higher boiling hydrocarbons, the supposition could not apply when the fuel is more volatile.

Callendar has suggested that there may be three types of 'knock' operative according to circumstances, namely, (1) the *pressure-wave* type, depending on the setting up of a pressure wave of sufficient intensity to fire the heated mixture, (2) the *nuclear* type, depending on the presence of nuclear drops or particles of relatively low ignition temperature, and (3) the *molecular* type, in which the temperature of a completely vaporised or gaseous mixture is sufficiently raised to induce direct molecular combination, even in the absence of pressure-waves or nuclei.

Quite recently * it has been suggested by Callendar and his collaborators who have been developing the 'nuclear-drop' theory that those fuels which give rise to 'knock' shew a tendency to form explosive peroxides as their primary oxidation products, and that such tendency is enhanced when the explosive medium contains liquid drops on whose surface oxygen may be condensed but is prevented by the presence of 'anti-knocks.' It is suggested that in engine explosions "the amount of peroxide formed would not in itself be sufficient to cause the detonation observed, but acts as a primer, causing simultaneous ignition of the drops. The metallic dopes ('anti-knocks') act by reducing the peroxides as fast as they are formed, and preventing their accumulation, thus delaying the ignition of the drops."

Two principal hypotheses—the one 'ionic' and the other chemical—have thus been advanced to explain 'knock,' and its prevention by 'anti-knocks'; but neither of them is free from difficulty, and as the subject is still in a very experimental and speculative stage, the wise will ponder and scrutinise carefully such facts as have been proven or alleged, but will keep an open-mind as to their interpretation.

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SECTION IV

CHAPTERS XXIV TO XXXIII

THE MECHANISM OF GASEOUS COMBUSTION

CHAPTER XXIV

THE INFLUENCE OF MOISTURE UPON COMBUSTION

In the year 1880 H. B. Dixon, in repeating Bunsen's experiments on the division of oxygen between carbonic oxide and hydrogen both present in excess, discovered that a mixture of carbonic oxide and oxygen dried by long contact with phosphoric anhydride will not explode when sparked in the usual way in a eudiometer over mercury, though the presence of a trace of moisture or of any gas containing hydrogen at once renders the mixture explosive.* These experiments, proving as they did the complexity of what outwardly seems one of the simplest cases of combustion, opened up a new field of scientific investigation and were truly epoch-making.

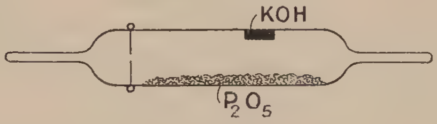

Fig. 131.

From the historical standpoint, it is well to recall how the original experiments, which were exhibited at the Swansea Meeting of the British Association in 1880, were actually carried out. A mixture of well-dried and purified carbonic oxide and oxygen in their combining proportions was kept at atmospheric pressure in a sealed tube fitted with firing wires (Fig. 131) over phosphoric anhydride for a week in order to dry the system thoroughly. On the walls of one of such tubes a small piece of solid potassium hydroxide had previously been fixed by fusion.

On passing a spark from a small induction coil across the firing wires no explosion resulted, but on applying heat externally to the portion of the tube in the neighbourhood of the caustic potash, whereby a minute quantity of water vapour was imparted to the gases, and again passing the spark, they instantly exploded.

Dixon also measured the average rate of propagation of flame between two points about a metre apart in a brass tube, 13 mm. in diameter, containing a $2CO + O_2$ mixture in different hygroscopic conditions as follows :

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* *British Association Reports*, 1880, p. 503; *Phil. Trans.* 175 (1884), p. 617.

TABLE LXXXIII.—INFLUENCE OF THE HYGROSCOPIC CONDITION OF A $2CO + O_2$ MIXTURE ON ITS MEAN RATE OF FLAME PROPAGATION (DIXON)

Condition of $2CO + O_2$ Mixture.	Average Velocity of Flame. Metres per sec.
Dried by slow passage over fresh P_2O_5 - - -	44
Dried by slow passage over previously used P_2O_5 -	69
Dried by slow passage over conc. H_2SO_4 - -	103
Saturated with aq. vapour at 6° C. - - -	125
Saturated with aq. vapour at 8° C. - - -	155
Saturated with aq. vapour at 12° C. - - -	200
Saturated with aq. vapour at 35° C. - - -	226

In 1883 H. B. Baker, working in Dixon's laboratory at Balliol College, Oxford, and afterwards at Dulwich College, found that highly purified charcoal, when heated to redness in carefully dried oxygen, burns with extreme slowness and without flame yielding principally the monoxide, the proportion of the dioxide formed varying inversely with the degree of dryness of the system.*

The charcoal used in the experiments had been prepared by carbonising sugar at red heat in a silver dish, the char being afterwards heated to redness for three days in a current of chlorine, then thoroughly washed with hot distilled water, and finally heated to redness in a vacuum. Some of it was sealed up in a glass tube filled with dry oxygen, the system being thoroughly dried by allowing it to stand in contact with phosphoric anhydride for several weeks. At the same time another portion of the charcoal was similarly sealed up in a tube filled with undried oxygen, and without the addition of any drying agent. On subsequently heating each tube strongly by the external application of a flame, the dry system shewed no visible sign of combustion, whereas in the undried active combination occurred with manifestation of flame.

In another series of experiments some of the highly purified charcoal was introduced into the well-cleaned glass tube *D* (Fig. 132), connected through one end with a series of three large flasks *A*, *B* and *C*, containing well-dried oxygen in contact with phosphoric anhydride over well-boiled *dry* mercury ; the other end of *D* was drawn out and bent into a ' delivery tube ' (as shewn), the end of which was sealed up. The glass tube connection through *C*, *B* and *A* led to a gas-holder containing pure P_2O_5-dried oxygen over strong sulphuric acid, which is not shewn in the diagram.

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* *Trans. Chem. Soc.* (1885), p. 349 ; also *Phil. Trans.* (1888), p. 571.

After the whole apparatus had stood for one or two weeks to allow of the system being well-dried in contact with the phosphoric anhydride, the sealed end of the delivery tube leading from *D* was nipped off under dry mercury in the trough *E*, and a eudiometer *F* full of dry mercury inverted over it. A slow current of the P_2O_5-dried oxygen was then passed over the charcoal in *D*, which was strongly heated by the external application of flame. It was found that although a very slow reaction occurred without any visible glow or flame, both the speed and the ratio between the CO_2/CO produced diminished as the drying progressed, thus :

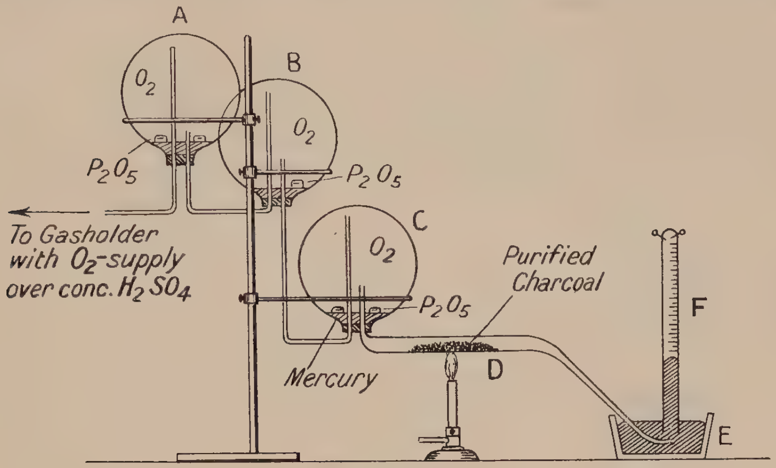

FIG. 132.

Drying Period.		One Week.	Two Weeks.	
			(i)	(ii)
Percentage Composition of the gases collected in F.	CO_2	5·0	2·2	1·7
	CO	40·0	39·5	27·8
	O_2	55·0	58·1	70·5

In further experiments H. B. Baker proved that highly purified dry sulphur or phosphorus could be repeatedly distilled in a glass apparatus filled with P_2O_5-dried oxygen without any combustion whatever occurring, although the admission of even a trace of moisture immediately caused a vivid burning. Moreover, in subsequent investigations, extending over a number of years up to the present, he has shewn that a large number of gaseous interactions are at least greatly assisted, even if they are not actually conditioned, by the presence of moisture. Thus, (1) a mixture of hydrogen and chlorine in stoichiochemical proportions, well-dried by contact with phosphoric anhydride, does not explode on exposure to sunlight as does an undried one ; (2) ammonia and hydrogen chloride, when similarly dried, do not combine when mixed in the cold ; whilst

(3) electrolytic gas, thoroughly dried over phosphoric anhydride and free from hydrocarbon impurity may be heated to redness, or exposed to ultra-violet light, without any measurable formation of water occurring.

The experiments with electrolytic gas, which were published in the year 1902, are of such outstanding interest in relation to our subject that they demand a detailed study. The reaction is a very sensitive one, and unless special precautions are taken the experiment is bound to fail. Baker used tubes of either hard Jena or hard Bohemian glass bent into the shape indicated in Fig. 133 *A*. Each tube was first of all cleansed with a mixture of nitric and chromic acids at 100° for twenty-four hours, after which it was washed out with distilled water and fitted to the tapered end of the platinum tube of a condenser. Purified water was then distilled through the tube for an hour; after allowing it to drain, it was dried out by heating it to

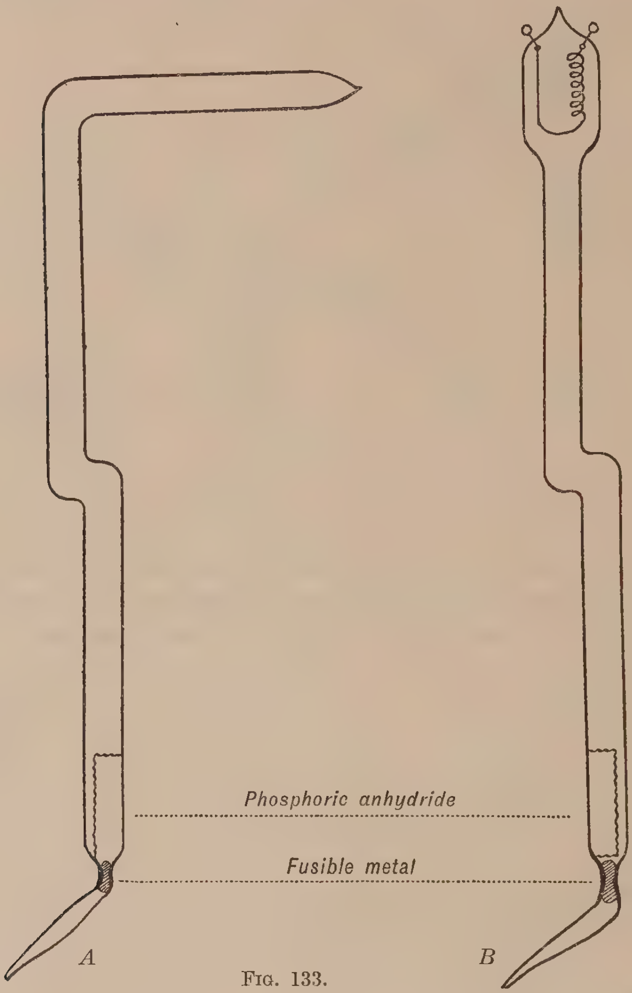

FIG. 133.

redness while a current of H_2SO_4-dried air was drawn through it. A plug of distilled phosphoric anhydride was introduced, the upper end of the tube drawn off, and the lower end drawn out to a capillary of about 0·5 mm. diameter. A small piece of fusible metal was introduced and the tube exhausted. It was then connected with the electrolytic apparatus in which a solution of fifteen times recrystallised barium hydroxide was being electrolysed, the resulting $2H_2+O_2$ mixture being roughly dried ' en route ' by passing it through a foot-long tube containing phosphoric anhydride. Comparative tubes were made at the same time from the same length of glass tubing, heated and filled in precisely the same way, except that no phosphoric anhydride was sealed up in them.

After ten days' drying two such tubes (one ' dry ' and the other ' wet ') were heated side by side in the same Bunsen flame. In twelve experiments the contents of the ' wet ' tube exploded, but those of the ' dry ' one did not. In each of the twelve experiments, when the 'dry' tubes were subsequently opened under mercury a very small contraction was observed in some cases, but mostly none at all. On introducing a small quantity of moisture the contents of each tube exploded when again heated in a flame.

In one experiment the 'dry' tube was fitted with a thin coil of silver wire attached by fusion to platinum wires, and the latter sealed through the hard glass wall. (Fig. 133 *B*.) The tube was then cleaned out, dried, and filled with the explosive mixture as before. After prolonged drying of its contents in contact with the phosphoric anhydride, the silver wire was heated electrically to its melting point without any explosion occurring, and no contraction was observed when the tube was afterwards opened under mercury. Some twenty more experiments were made to determine whether electric sparks could be passed through the dried mixture without explosion, but only in one case was this accomplished, and then only with ' extremely small sparks.'

The foregoing discoveries were of great fundamental importance, and have given rise to much discussion among chemists without, however, any general agreement about their inner meaning having been reached, although within recent years the main issues have been narrowed. For a proper understanding of the position to-day it is important first of all to consider the proven *facts,* without any bias, and to regard as tentative only any view of them which we may feel warranted in forming, because new evidence is coming out, and the matter is not yet *une chose jugée.* It can, however, be said that whereas experiments have proved that the removal of moisture from many (but not all) gaseous systems increases in an extraordinary degree their resistance to chemical change, they cannot yet be said to have proved, as is sometimes supposed, that the presence of moisture is *absolutely essential* to chemical change in such cases.

Whichever way, however, the final verdict may go, the equally important question of *how* the moisture either assists or conditions the chemical change would still need answering. Some of the new evidence referred to will be discussed in a later chapter in which the combustion of carbonic oxide will be fully dealt with. In this one we will give a more general survey of the outstanding facts, as known up to the end of the year 1924, without referring to the theories founded on them.

It has already been explained in Chapter VI. (*q.v.*) how Dixon's discovery of the influence of moisture upon the combustion of carbonic oxide led to an understanding of Bunsen's failure in 1853 to verify the operation of the law of mass action in his explosion experiments upon the division of oxygen between carbonic oxide and hydrogen when the combustible gases are present in excess. For in the year 1884 Dixon published his memoir on "Conditions of Chemical Changes in Gases," * in which he shewed that when a *dry* mixture of carbonic oxide and hydrogen with defect of oxygen is exploded, under conditions which will prevent condensation of steam during the cooling period, the ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ in the products is independent of the proportions of the constituents in the original mixture fired, a conclusion which was independently confirmed by Horstmann in Germany about the same time. What really happens in such a case is that the oxygen divides itself in the flame between the two combustible gases, and then, as the products cool down, the reversible reaction $CO + OH_2 \rightleftharpoons CO_2 + H_2$ comes into play, the equilibrium ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ adjusting itself automatically with the falling temperature, in accordance with the law of mass action, until a point is reached when it can no longer do so, with the result that the equilibrium condition at that temperature is, so to speak, 'frozen out.'

Dixon found the aforesaid ratio to be 4·0, which probably represents the equilibrium condition at some unknown point above 1500° C. on the cooling curve of the exploded gases at which the adjustment of the equilibrium with temperatures had ceased to keep pace with the rate of cooling.†

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* *Phil. Trans.* (1884), pp. 617 to 684.

† Experiments published by O. Hahn in 1903 (*Zeit.Phys. Chem.* **43**, p. 705, and **44**, p. 573) shewed that between 786° and 1405° C. the equilibrium constant '*K*' for the system $\frac{CO \times OH_2}{CO_2 \times H_2}$ varies with temperature as follows:

Temperature °C.	*K.*
786°	0·81
886°	1·19
986°	1·54
1086°	1·95
1205°	2·10
1405°	2·49

How exceedingly small is the amount of moisture which 'makes all the difference' in the already cited cases of combustion may be gathered from an estimate made many years ago by E. W. Morley that the mere passing of a gas slowly through a long column of phosphoric anhydride leaves in it only 3 milligrams of water-vapour per million litres (*i.e.* less than 4 molecules of steam per 1000 million molecules of gas); * yet a much more rigid and prolonged drying is usually required to demonstrate the comparative inertness of two gases which, in the presence of moisture, will combine quite readily. This has always constituted a great difficulty in the way of explaining from a kinetic standpoint how the water really functions in such cases.

It should also be observed that, in addition to the rigid drying required, it is essential to ensure by every possible precaution, not only that the gases employed are purified in the highest degree, but also that the inside surfaces of the containing vessels are absolutely clean, and that in no possible way can any trace of organic impurity contaminate the system; especially important is it to ensure that all stopcocks used in the apparatus are lubricated with an inorganic substance such as syrupy phosphoric acid. For the neglect or relaxation of any such precaution will involve the risk of failure, which may be seriously misleading. Indeed, the successful conduct of such experiments demands infinite patience, care and vigilance on the part of the operator, and no one should be entrusted with them who has not become thoroughly familiar with the elaborate experimental ritual necessarily involved.

As far back as 1886 Lothar Meyer, in repeating H. B. Dixon's original experiments, found that a $2CO + O_2$ mixture which had been dried by contact with phosphoric anhydride for six days in a eudiometer over mercury, and which was not ignited at 156 mm. pressure by a Rhumkorff spark of low intensity, could be made to combine non-explosively by passing through it a more powerful spark continually for two minutes, combustion being complete.† Probably the degree of dryness attained in this experiment would not be considered to-day sufficient to warrant any definite conclusion being drawn from it, but it is interesting to recall that Lothar Meyer was led by it to express the view that a far higher temperature is required to initiate the interaction between carbonic oxide and oxygen than between carbonic oxide and steam.

As time went on, other facts were discovered which tended to throw doubt upon the extreme doctrine that carbonic oxide and oxygen *are in all circumstances* incapable of combining directly. Indeed, as early as 1886 H. B. Dixon had observed that "*in the explosion of cyanogen with an excess of oxygen, the formation of carbonic acid is complete, and is not affected by the presence of moisture.*" ‡ Ten years later, in conjunction with E. H

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* *Amer. Journ. Sci.* 34 (1887), p. 199; and *J. Amer. C.S.* 26 (1904), p. 1171.

† *Berichte*, 19 (1886), p. 1099.

‡ *Trans. Chem. Soc.* 49 (1886), p. 390.

Strange and E. Graham, he found that, contrary to expectations, the flame produced by the explosion of a well-dried mixture of cyanogen with twice its own volume of oxygen, when analysed photographically upon a rapidly-moving film, " *does not appear to differ from the flame given by the same gases mixed with* 1·5 *per cent. of water,*" from which observation he concluded that " *in a mixture of freshly-formed carbon monoxide and oxygen, these gases unite as the mass cools down without the intervention of steam ; and where steam is present it does not appreciably alter the time during which the change continues.*" *

In this connection also it may be recalled how, when in 1894 Smithells and Dent examined in their ' separator ' the flame of a P_2O_5-dried mixture of cyanogen with sufficient air to give a separation of the two cones, they found that, with the cones widely separated, the upper one, in which the combustion was almost wholly that of carbon monoxide to dioxide, was immediately extinguished by bringing a bottle of dry air over it ; but that " on approximating the two cones a point was soon reached where it was impossible any longer to extinguish the outer cone by such means." This very interesting result, together with that previously recorded by Dixon, certainly suggested that carbonic oxide will combine directly with oxygen, provided that it is *freshly formed* in a flame, and presumably in an ' activated ' and ' ionised ' condition.

In 1903 A. F. Girvan, in describing certain experiments which he had made to see whether the drying of an explosive mixture of carbonic oxide and oxygen by exposure to low temperature, produced by either liquid air or solid carbon dioxide in alcohol, would be sufficient to prevent chemical union when it was sparked after regaining the room temperature, made some important new observations.† He found that whereas a series of ' powerful sparks ' from an induction coil would not ignite a mixture which had previously been dried at either – 180° or – 80° C., they would always do so when the mixture had been dried at a temperature between – 50° and – 35° C., whilst a single spark would always cause an explosion if the drying had been at – 15° C. only. He also remarked that " the explosion produced by powerful sparks in the gases dried between – 50° and – 35° C. is of a very different character from that obtained with the wet gases ; the latter is very quick and violent, and gives a metallic click, but the former takes place quietly, and the explosive wave travels quite slowly along the tube."

During the long course of his researches upon the subject, H. B. Dixon has more than once endeavoured to determine whether the presence of ' nascent-oxygen ' would suffice to cause carbonic oxide to burn in the absence of moisture from the system. Thus in 1896 he was led to try the effect of a spark on a mixture of carbonic oxide with ozonised oxygen dried by a week's contact with phosphoric anhydride. Notwithstanding that the mixture contained 36 per cent. of carbonic oxide, 8 per cent. of ozone, and 56 per cent. of oxygen, a spark passed through it between wires 7 mm. apart produced no explosion, although "a considerable halo of blue light" appeared round its path.* In the following year, in conjunction with E. J. Russell, he succeeded in carrying out some very bold experiments, in which a mixture of 60 per cent. carbonic oxide, 29 per cent. chlorine peroxide, and 11 per cent. oxygen, dried by contact with phosphoric acid for six or fifteen days, was sparked. In both cases, although a pale blue flame traversed the tube, and there was sufficient chlorine peroxide present to burn it all, the greater part of the carbonic oxide remained unburnt, a result which Dixon thought did "not favour the view that oxygen just liberated from a compound is more active than ordinary oxygen in attacking carbonic oxide at a high temperature." †

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* *Trans. Chem. Soc.* 69 (1896), p. 773.

† *Proc. Chem. Soc.* 19 (1903), pp. 236–238 ; unfortunately no fuller account of the experiments appear to have been published.

In view of some of the extreme views which have been advanced concerning the function of moisture in combustion, attention should be directed to certain cases—namely, those of cyanogen, of carbon disulphide and of hydro-carbons (*e.g.* ethylene and acetylene)—in which combustion does not seem to depend upon the presence of moisture; because, if a broad view of the matter is to be taken, such facts ought not to be ignored. The case of cyanogen having already been referred to, we need now only consider those of carbon disulphide and the hydrocarbons.

In 1888 H. B. Baker shewed that carefully dried and purified carbon disulphide explodes with dry oxygen just as readily as when moist.‡ In 1899 this result was confirmed by H. B. Dixon and E. J. Russell, who reported as follows: § "Using the purest carbon disulphide we were able to prepare, we made mixtures with oxygen and nitrous oxide in varying proportions, and allowed them to dry over phosphorus pentoxide for periods varying from a fortnight to eighteen months. In every case there was an explosion, and combustion was complete. When dried mixtures of carbon disulphide and carbon monoxide with oxygen were sparked, it was always found that the carbon monoxide was largely unburnt whilst the carbon disulphide burnt completely. The union of the carbon disulphide and oxygen thus occurs when the gases have been brought to a state of dryness in which carbon monoxide and oxygen are incapable of burning."

Dixon and Russell obtained further evidence in support of this conclusion by a comparison of the rates of explosion of wet and dry mixtures, their point being that "if moisture is necessary for combustion, the velocity of explosion in a mixture of moist gases should be greater than in a mixture of dry gases," but it was found actually to be less, as the following results show :

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* *Trans. Chem. Soc.* 69 (1896), pp. 785–786.

† *Trans. Chem. Soc.* 71 (1897), pp. 601–607.

‡ *Phil. Trans.* 179 (1888), p. 582.

§ *Trans. Chem. Soc.* (1899), pp. 601 to 602.

Mixture.	Rate of Explosion in Metres per sec. for	
	Dried Gases.	Gases Saturated with Moisture at 15° C.
CS_2+3O_2	1802	1755
CS_2+5O_2	1732	1672

The case of hydrocarbons was investigated by W. A. Bone and G. W. Andrew in 1906.* Ethylene and acetylene were selected for the test, because of the fact that no steam is produced during the initial stage of their slow combustion, as is the case with paraffins. The experimental method consisted in (1) preparing each of the two hydrocarbons in a high degree of purity, the chemically purified gas being in each case finally subjected to repeated liquefaction or solidification in a small glass bulb immersed in liquid-air and subsequent fractional vapourisation of the liquid or solid; (2) mixing each with an equimolecular proportion of pure oxygen, prepared by carefully heating recrystallised potassium permanganate; (3) filling with the mixture a series of Jena borosilicate glass tubes (length = 70 cm., diameter = 15 cm., capacity = 150 c.c.), bent into the form shewn in Fig. 134, each of which had been carefully cleaned out and dried according to the most approved manner; (4) thoroughly drying the mixture admitted to one set of such tubes (*a*) by passing it through a long column of redistilled phosphoric anhydride, and (*b*) then sealing it up in each tube at room temperature and pressure in contact with redistilled phosphoric anhydride, and allowing several weeks for the drying operation to be completed; (5) filling another set of such tubes with the same experimental mixture, after passing it slowly over the surface of distilled water, and sealing them up at room temperature and pressure

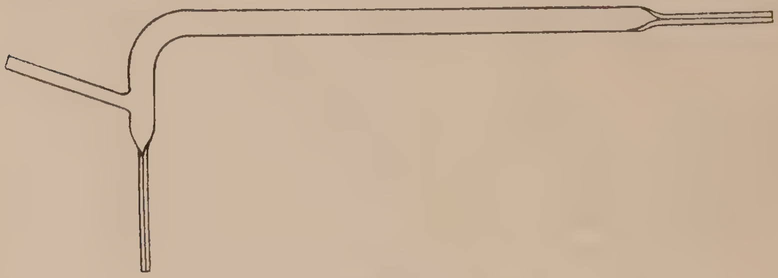

FIG. 134.

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* *Trans. Chem. Soc.* **89** (1906), pp. 652 to 659.

without introducing any drying agent; and finally (6), comparing the behaviour of the *dried* and *undried* mixtures respectively, when each tube was subjected to precisely the same degree and duration of heat in a Lothar Meyer constant temperature furnace. For further details of the experimental procedure and results the original paper should be consulted. The results revealed no material difference between the behaviours of the dried and undried mixtures; sometimes indeed the dried mixtures reacted rather more quickly than the undried.

The results of *two* comparative sets of experiments with an equimolecular mixture of ethylene and oxygen may be quoted as typical examples. In each of the 'dry' experiments the 'drying period' extended over eleven weeks. On subsequently comparing the temperatures at which any visible reaction (formation of a white-film of para-formaldehyde in the vertical cool end) commenced when the horizontal limb of each tube was heated in the furnace, they were found to be the same (385°–398° C.) in both the case of the 'dried' and the 'undried' system; moisture first appeared about five minutes later in each case; finally, after continuing the heating for fifteen minutes longer in each case (maximum temperature = 430° to 450° C.), the tubes were withdrawn from the furnace, cooled, and their gaseous contents analysed, with the following results:

Table LXXXIV.—Influence of Moisture on the Slow Combustion of a $C_2H_4 + O_2$ Mixture (Bone and Andrew)

Mixture.	Percentage Contraction on Cooling.	Percentage Composition of the Gaseous Products.					
		CO_2.	CO.	C_2H_4.	C_2H_6.	H_2.	O_2.
(1) P_2O_5-dried 11 weeks	37·0	10·25	45·75	32·65	2·10	1·05	8·20
	37·7	10·25	44·50	28·85	6·35	4·00	6·05
(2) Undried	34·8	10·60	48·4	27·6	4·65	2·70	6·05
	36·1	11·45	50·8	24·85	5·15	3·25	4·50

Finally, in order to test the efficiency of the drying arrangements used in the 'dry' series, a corresponding set of comparative experiments was made, in precisely the same manner, with pure electrolytic gas, using the same reaction tubes and drying arrangements, but allowing (in the 'dry' series) only four weeks for the drying over the redistilled phosphoric anhydride. An enormous difference, was, however, found between the behaviour of the 'moist' and 'dried' systems when they were afterwards subjected for ten minutes to a temperature of 525° C. in the Lothar Meyer furnace. In cases of the undried gases, water invariably appeared in the cold ends of the tubes after 1½ minutes, and accumulated as the heating was continued; altogether between 40 and 50 per cent. of the gases combined. In case of the P_2O_5-dried gases, however, there was never any visible sign of combination, and on subsequently opening the cooled tubes under mercury the observed contractions were either *nil* or less than 3 per cent. of the original volume. The results of the two series of control experiments are contrasted as follows :

TABLE LXXXV.—INFLUENCE OF MOISTURE ON THE COMBUSTION OF ELECTROLYTIC GAS (BONE AND ANDREW)

Experiment Number.	Percentage Combination observed in	
	Dry Series.	Undried Series.
1	0·5	52
2	3·0	45
3	*nil*	42
4	3·0	40

Therefore, the experiments shewed that a degree of P_2O_5-drying such as practically inhibited the combustion of electrolytic gas made no material difference in the case of the equimolecular highly purified hydrocarbon-oxygen mixtures examined.

It has also been found recently in our Research Laboratories at the Imperial College that an equimolecular mixture of highly purified ethylene and oxygen ($C_2H_4 + O_2$) rigidly dried for three weeks in contact with phosphoric anhydride initially propagates flame at a speed about 30 per cent. faster than does the same mixture when saturated with moisture at the room temperature.

In this chapter we have purposely refrained from entering into any discussion of the various theories which have been advanced to explain the function of steam in those cases where experiments have shewn it to be operative, deeming it more important at this stage for the reader to get the outstanding facts clearly in mind. In a subsequent chapter we shall return to the subject, when dealing further with the combustion of carbonic oxide.

CHAPTER XXV

THE COMBUSTION OF CARBON AND ITS INTERACTIONS WITH STEAM

The Combustion of Solid Carbon

ALTHOUGH the combustion of solid carbon has been studied by chemists for upwards of a century there is still no general agreement among them as to what is the immediate product of the action of oxygen upon it.

In view of the fact that a diamond burns when strongly heated in oxygen forming carbon dioxide *without any visible flame*, it was formerly almost universally believed that such is the initial interaction, the monoxide subsequently resulting only when the primary product comes in contact with an excess of incandescent carbon, thus :

$$(1)\quad C+O_2=CO_2,$$
$$(2)\quad CO_2+C=2CO.$$

The correctness of this view, which is still prevalent in technical literature, was challenged in 1872 by the late Sir Lowthian Bell, who as the result of his classical investigations upon the chemical phenomena of iron smelting advanced some very ingenious, if not altogether conclusive, arguments in support of his opinion that " carbon monoxide and not carbon dioxide is the chief, if not the exclusive, and immediate action of the hot blast on the fuel " (*i.e.* on the coke) in the blast furnace.

In the year 1887 C. J. Baker made experiments to ascertain the nature of the gases produced by heating carbon which had previously absorbed oxygen at low temperatures. He found that whereas *moist* oxygen which had been absorbed at – 12° C. was evolved as carbon dioxide at 100°, the effect of *thoroughly drying* the materials by means of phosphoric anhydride was to cause the gas to be retained until a temperature of 450° was reached, when it was evolved chiefly as carbon monoxide. Hence he concluded that carbon is burned directly to the monoxide by absorbed oxygen.

The work of H. B. Baker in the following year on the subject which has been described in the previous chapter (*q.v.*) led him to conclude not only that moisture facilitates the combustion of carbon but also that " carbon burns first to carbon monoxide." He also shewed that, *in absence of moisture*, carbon dioxide is not reduced by carbon even at bright red heat.

This new evidence was at the time accepted as conclusive by most British chemists, but when in 1891 Mendeléeff, in his *Principles of Chemistry* (English ed., vol. i. p. 388), adopted the older view that "the first product of the combustion of charcoal is always carbonic anhydride and not carbonic oxide," * the controversy was reopened. The Russian chemist seems to have based his opinion upon the results of a series of experiments published by Lang in the year 1888 † in which oxygen (*dry*) was passed at different regulated velocities through a glass tube packed with purified wood-charcoal and maintained in a furnace at 500° C., *at which temperature Lang asserted that carbon does not reduce its dioxide.* From the following results it will be seen that the proportion of carbon monoxide found in the exit gases diminished with the stream velocity, until in one experiment with a very slow stream it entirely disappeared. Lang ascribed the formation of the monoxide in the experiments with the faster gas streams to the occurrence of local heating which, he argued, was sufficient to effect some reduction of the dioxide.

TABLE LXXXVI.—LANG'S FIRST SERIES OF EXPERIMENTS

Time required to collect 100 c.c. of Gases.	Percentage Composition of the Resulting Gases.		
Minutes.	CO_2	CO.	N_2.
2	89·4	8·4	2·2
4	90·0	7·8	2·2
10	90·4	7·2	2·4
20	91·4	6·1	2·5
25	92·5	5·3	2·2
60	94·3	3·0	2·7
240	96·2	*nil*	3·8

In a second series, Lang passed a mixture containing 77·7 per cent. of oxygen, 18·5 per cent. of carbon monoxide, and 3·8 per cent. of nitrogen at different velocities over purified carbon at 500° C. with the object of ascertaining (1) whether with a slow stream, and in the absence of local heating, the oxygen could be directly transformed into its own volume of carbon dioxide without increasing the proportion of monoxide in the flowing gases, and if so, then (2) what would be the effect of increasing the velocity of the gases until the local heating was sufficient to make the carbon glow. The results observed in three groups from experiments are shown below :

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* It may be noted that this statement is repeated on p. 423 of the third English edition published in 1905, and on p. 421 of the same edition it is also stated that carbonic oxide "is formed whenever the combustion of organic substances takes place in the presence of a large excess of incandescent charcoal; the air first burns the carbon into carbonic anhydride, but this in penetrating through the red-hot charcoal is transformed into carbonic oxide, $CO_2 + C = 2CO$."

† *Zeit. Phys. Chem.* (1888), p. 161.

TABLE LXXXVII.—LANG'S SECOND SERIES OF EXPERIMENTS. TEMPERATURE = 500° C.

	Time required to collect 100 c.c. of Gases.	Percentage Composition of the Resulting Gases.			Observations.
	Minutes.	CO_2.	CO.	N_2.	
Group 1.	120 150	78·0 77·9	18·3 18·4	3·7 3·7	No local heating. No change in CO content; O_2 replaced by CO_2.
Group 2.	1 1 20 secs.	71·2 70·8 39·6	24·7 25·0 56·4	4·1 4·2 4·0	No visible flame. Increase in CO due to reduction of CO_2 by C.
Group 3.	10 secs. 5 ,,	86·4 88·4	9·8 8·0	3·8 3·6	Carbon glowed. Flame of CO visible.

Assuming that carbon does not appreciably reduce its dioxide at 500° C. Lang claimed to have proved that in the burning of carbon the formation of the dioxide precedes that of the monoxide (" *durch das Zusammentreffen des Sauerstoffs mit der Kohle ensteht zuerst Kohlendioxyd* ").

H. B. Dixon subsequently repeated and criticised Lang's principal experiments,* finding that some monoxide, as well as the dioxide, is always produced when oxygen is passed over purified coke at 500° C. no matter how slow the gas stream may be, although it was impossible to say that no local heating occurred in the experiment. (Table LXXXVIII.)

TABLE LXXXVIII.—H. B. DIXON'S EXPERIMENTS ON THE ACTION OF OXYGEN UPON COKE AT 500° C.

No.	100 c.c. of Gas collected in Minutes.	Percentage Composition of Product.			
		CO_2.	CO.	O_2	N_2.
1	3·5	80·83	16·7	—	2·99
2	23	87·52	9·48	0·25	2·74
3	120	96·38	1·42	0·26	1·93
4	240	96·52	0·41	0·21	2·17

On repeating Lang's second series of experiments (*q.v.*), Dixon found that when mixtures containing from 75 to 80 per cent. of oxygen and from

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* *Trans. Chem. Soc.* 75 (1899), p. 630.

25 to 20 per cent. of carbonic oxide were passed over coke at 450 to 500° C., the amount of carbonic oxide in the products increased with the velocity of the gas-stream until a maximum was reached when 100 c.c. were collected in about 5 or 6 minutes. With quicker velocities the carbonic oxide diminished again, but with a very slow gas stream only a small quantity of it escaped combustion. He regarded the results of his experiments with *slow* gas streams as being ' entirely at variance ' with those of Lang under similar conditions.

He, therefore, considered that his experiments threw doubt on the validity of Lang's conclusions, but that, whereas Baker's work had greatly added to the weight of evidence in favour of the view that carbon burns in the first instance to carbonic oxide, " it must be admitted that a decisive proof is still required."

Within recent years the subject has been thoroughly reinvestigated by Rhead and Wheeler over a range of temperature extending from 100° up to 900° C.* A preliminary series of experiments, in which either air or oxygen was circulated over highly purified wood-charcoal maintained at various selected constant temperatures between 250° and 500° C., failed to afford any conclusive evidence of the *exclusive* primary formation of either the monoxide or the dioxide, and led to the conclusion that both are produced *simultaneously*.

Further investigation over a much wider range of temperature afforded much presumptive evidence in favour of the view that neither the one nor the other of the two oxides is initially formed, but that both are *simultaneously* produced as the result of the decomposition of an unstable ' physicochemical complex,' C_xO_y, which (according to this theory) should be regarded as the immediate and initial product of the action of oxygen upon carbon.

This view of the matter undoubtedly reconciled a good many well-established facts, which otherwise appeared conflicting, and it may be provisionally adopted as a working hypothesis until more is known concerning the mechanism of oxygen-fixation by carbon in the absence of water vapour. Some recent, and as yet unpublished, work by M. Shah in H. B. Baker's laboratory suggests that the *initial* stage of the combustion of charcoal by either oxygen or nitrous oxide involves merely a ' fixation ' of oxygen rather than the formation of any definite C_xO_y complex.

In the case of an ordinary incandescent coke fire through which air is being drawn, it seems probable that the sequence of events is (i) a ' fixation ' of oxygen at the carbon surface, (ii) the simultaneous evolution therefrom of oxides of carbon, and (iii) the rapid attainment and adjustment of a mobile equilibrium in the reversible system,

$$2CO \rightleftharpoons C + CO_2,$$

in consonance with the temperature in each successive layer as the mixed

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[*] *Trans. Chem. Soc.* 101 (1912), pp. 101, 846 ; and 103 (1913), pp. 103, 461.

gases ascend through the fire. Also, and especially in such regions where the atmosphere in the spaces between the porous coke masses contains free oxygen, some combustion of carbon monoxide may occur, in which case the aforesaid equilibrium must be continuously adjusting itself, both to variations in the relative concentrations of the two oxides of carbon. as well as to the temperature changes. Consequently, the lower region of the fire must be the seat of a complex play of chemical forces which, however, may be regarded as always subject to the laws governing the attainment of mobile equilibrium in the reversible system formed by carbon and its two oxides.

The Reversible System $2CO \rightleftharpoons C + CO_2$

The investigation of the effects of temperature and pressure upon equilibrium in this system was also carried out very thoroughly by Rhead and Wheeler,* whose work in this connection must be acknowledged as having surpassed in point of carefulness and accuracy that of any previous investigators.

According to Le Chatelier's extension of Van't Hoff's well-known principle of mobile equilibrium in such a system, any change in the factors of equilibrium (*e.g.* active masses, pressure and temperature) from outside must be followed by a reverse change within the system. Thus, for example, (1) inasmuch as any change in the direction $2CO = CO_2 + C$ is accompanied by a decrease in volume, an increase in pressure at any given temperature will cause a decrease in the 'equilibrium' proportions of carbon monoxide, and *vice versa* ; also (2) inasmuch as any change in the said directions must be exothermic, an increase in temperature at any given pressure will cause an increase in the 'equilibrium' proportion of carbon monoxide.

The law governing equilibrium in such a reversible system may be expressed by the following general formula :

$$500\int L\frac{dT}{T^2} + (N' - N)\log_e P + \log_e \frac{C_1^{n_1} . C_1'^{n_1'}}{C_2^{n_2} . C_2'^{n_2'}} \ldots = K,$$

where

L = the total heat of the reaction at the absolute temperature T ;

P = the pressure in atmospheres ;

N' and N = the number of gaseous molecules in the left and right hand side respectively of the equation ;

n_1, n_1' and n_2, n_2' = the number of molecules of the different gases participating in the reaction ;

C_1, C_1' and C_2, C_2' = the corresponding concentrations (active masses).

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* *Trans. Chem. Soc.* 97 (1910), 2178 ; and 99 (1911), 1141.

Thus, in the particular case of $2CO \rightleftharpoons C + CO_2$ under discussion, assuming L to be constant and equal to 39 K.C.US. at all temperatures, and P to be 1 atmosphere, the equation becomes,

$$\frac{19500}{T}+\log_e\frac{C_1^2}{C_2}=K,$$

where C_1 and C_2 represent the concentrations of the CO and CO_2 respectively.

According to Rhead and Wheeler's results, the value of K progressively increases from 19·85 at 800° C. (1073° A.) to 20·17 at 1100° C. (1373° A.), which circumstance may be ascribed to some decrease with temperature of the value of L, consequent upon a corresponding change in the specific heats of the two sides of the system. Or, if constants be introduced into the equation to allow for this, it may be written in the form :

$$\frac{1}{2}\cdot\frac{38055+2{\cdot}02T-0{\cdot}0031\,T^2}{T}+\log_e P+\log_e\frac{C_1^2}{C_2}=18{\cdot}75,$$

from which the relative concentrations C_1 and C_2 corresponding to any particular absolute temperature or pressure, P, may be calculated.

According to Rhead and Wheeler's experiments, the velocity at which carbon dioxide is reduced by carbon at temperatures above red heat is always many times (*e.g.* at 850° C. 166 times) faster than that at which CO is dissociated at the same temperature. The condition of equilibrium, when P (*i.e.* the combined partial pressure of the CO and CO_2) = 1 atmosphere, was found experimentally to vary with the temperature as follows :

Temperature.	Relative Percentages of	
°C.	CO_2	CO.
850	6·23	93·77
900	2·22	97·78
950	1·32	98·68
1000	0·59	99·41
1050	0·37	99·63
1100	0·15	99·85
1200	0·06	99·94

whilst the variations with pressure at 1000° C. was found to be as follows :

Pressure	Relative Percentages of	
Atmospheres.	CO_2.	CO.
3·78	3·17	96·83
2·67	2·18	97·82
1·14	1·17	98·83
0·66	0·65	99·35

and at 1100° C. :

Pressure	Relative Percentages of	
Atmospheres.	CO_2.	CO.
3·65	0·92	99·08
2·25	0·60	99·40
1·33	0·35	99·65

Supposing, for the moment, that the time required for the attainment of equilibrium in the system $2CO \rightleftharpoons C + CO_2$, at such temperatures (say 1000° C. and upwards) as prevail in the lower layer of a furnace fire, is comparable with the time during which the upward flowing gases are actually in contact with the incandescent carbon, the *net* immediate result of the combustion will, for all practical purposes, be CO and not CO_2. And inasmuch as the rate at which CO is dissociated into C and CO_2 at lower temperatures (say 850° to 1000°) is many times less than that at which the reverse change occurs, practically all the carbon monoxide formed in the first instance will survive as such unless and until it meets and is burnt by a secondary oxygen supply. Hence, for all practical purposes, it may be regarded as established that, at the temperatures ordinarily prevailing in a coke furnace fire, the carbon is burnt to the monoxide in the first instance, although, theoretically, in no circumstances can the dioxide be entirely absent.

The Interaction of Steam with Incandescent Carbon

In incomplete combustion and flames generally, in which hydrocarbons or ordinary gaseous fuels are being burnt, such an important *rôle* is played by steam in its interactions with carbon or carbonic oxide that some reference must be made to them in connection with the subject of flame reactions.

The interactions between steam and carbon are of course endothermic. At low temperatures (500° to 600° C.), the chief products are carbon dioxide and hydrogen, according to the equation :

$$(a)\ C + 2H_2O = CO_2 + 2H_2 \ldots - 19{\cdot}0\ \text{K.C.Us.},$$

whereas, at temperatures of 1000° C. and upwards, the main result is the production of equal volumes of carbon monoxide and hydrogen, the so-called 'water-gas' reaction, as follows :

$$(b)\ C + H_2O = CO + H_2 \ldots - 29{\cdot}0\ \text{K.C.Us.}$$

At intermediate temperatures, the products correspond with the simultaneous occurrence of both reactions, the second gradually asserting itself as the temperature rises, until, at 1000° C., it almost entirely supersedes the first. Hence, in flames it is only the second one that need be considered. In the manufacture of 'water-gas' and 'producer-gas,' however, both reactions play a part.

The Influence of the Reversible System $CO+OH_2 \rightleftharpoons CO_2+H_2$ *in Flames*

Whenever, as the result of incomplete combustion, the oxides of carbon, steam and hydrogen are present simultaneously in flames, they constitute an active reversible system:

$$CO+OH_2 \rightleftharpoons CO_2+H_2 \ldots +10 \text{ K.C.US.},$$

whose dynamic equilibrium may be defined in terms of the relative concentrations of the reacting gases and the absolute temperature, thus:

$$\frac{CO \times OH_2}{CO_2 \times H_2}=K.$$

On thermodynamical grounds it may be predicted that the value of K will increase with the temperature, since the equilibrium in a reversible system shifts with rising temperatures in the direction of negative heat change. This conclusion was verified experimentally in the year 1903 by Oscar Hahn,* who shewed that between 786 and 1405° C. the values of 'K' are as follows:

Temp. °C.	*K*.	Temp. °C.	*K*.
786°	0·81	1086°	1·95
886°	1·19	1205°	2·10
986°	1·54	1405°	2·49

Hahn also subjected the reaction to a thermodynamical analysis in the light of his experimental results, deducing the equation:

$$\log K=-2232/T-0{\cdot}08463 \log^{10} T-0{\cdot}0002203T+2{\cdot}5084,$$

when T = the absolute temperature.

From this equation the following values of K would be predicted:

Temp. °C.	1005°	1205°	1405°	1600°
K	1·63	2·54	3·43	4·24

Later on Haber, in conjunction with Richardt and Allner, determined the 'water-gas equilibrium' in open flames, finding values between 1250° and 1500° C. which agreed throughout with those predicted by Hahn's equation, so that it may be accepted as reliable at any rate up to the last-named temperature.†

In the previous chapter it was shewn how in 1884 H. B. Dixon found an equilibruim ratio $K=4{\cdot}0$ for the products when various dried mixtures of carbonic oxide and hydrogen in defect were exploded over mercury in a dry eudiometer under conditions which prevented any condensation of steam during the cooling period. In 1905 G. W. Andrew, working in Bone's laboratory in Manchester on the water-gas equilibrium in hydrocarbon flames,* obtained K values very near to 4·0 for systems containing the oxides of carbon, hydrogen, and steam produced in hydrocarbon-oxygen explosions where combustion was incomplete but no carbon deposited, as the following figures indicate :

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* *Zeit. Phys. Chem.* **43**, p. 705; and **44**, p. 513.

† F. Haber, *Thermodynamics of Gas Reactions* (1908), p. 142.

Mixture Exploded.	Mean K for Cooled Products $\frac{CO \times OH_2}{CO_2 \times H_2}$
$CH_4 + O_2$	3·98
$2CH_4 + 3O_2$	3·98
$2C_2H_6 + 3O_2$	4·12
$2C_2H_6 + 5O_2$	3·63
$2C_2H_4 + 5O_2$	3·47

It should be mentioned that subsequently W. A. Bone and collaborators, in experiments where a series of mixtures containing methane and hydrogen (or carbonic oxide) were exploded with defect of oxygen at high pressures in steel bombs under conditions such that no carbon was deposited, obtained 'K'-values mostly between 3·0 and 4·0, though a few were lower.†

From such results it seems probable that when a system containing the oxides of carbon, hydrogen and steam only is cooling down as the result of incomplete combustion in gaseous explosions, the equilibrium ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ will adjust itself automatically with the falling temperature until a point somewhere between 1400° and 1600° C is reached, after which no further adjustment will occur. And in this conclusion we are supported by F. Haber, who, in writing about the equilibrium conditions in Bunsen flames, remarked that: "Above 1200° equilibrium is reached. The equilibrium is not perceptibly displaced during the period of cooling if the temperature does not exceed 1500°. If the flame is hotter than this, the equilibrium is progressively displaced until the gas cools to 1500°, when the equilibrium 'freezes,' to use our earlier expression." ‡

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* *Trans. Chem. Soc.* **105** (1914), pp. 444–456.

† *Phil. Trans.* A. **215** (1915), 275 to 318.

‡ *Thermodynamics of Gas Reactions* (1908), p. 309.

CHAPTER XXVI

THE FLAME SPECTRA OF CARBONIC OXIDE, HYDROGEN, AND WATER-GAS

Before discussing the various theories which have been advanced regarding the influence of moisture upon the combustion of carbonic oxide, it is advisable to consider what spectroscopic analysis, the most fundamental of all tests, reveals.

In the years 1923–5 F. R. Weston, who then held the Gas Light and Coke Company's Research Fellowship in the Department of Chemical Technology at the Imperial College of Science and Technology, London, was set to make a systematic investigation of the flame spectra of carbonic oxide, hydrogen, and mixtures of the two in varying proportions, under the joint supervision of Professors W. A. Bone and A. Fowler, because it was felt that such evidence was needed for the further elucidation of the subject. His results, which subsequently were published in two papers communicated to the Royal Society,* will be considered in this chapter, although the reader is recommended to consult the original papers in which a wider selection of the photo-spectrograms is reproduced than is possible here.

No observant person familiar with the flames of carbonic oxide and hydrogen can fail to be impressed by the striking contrast there is between their outward appearances. Judged by the eye, the beautiful lambent blue flame of carbonic oxide in air seems quite different from the hardly visible 'sharp' flame of hydrogen. It is also well-known that the flame of 'water-gas,' which chiefly consists of nearly equal volumes of carbonic oxide and hydrogen, resembles that of hydrogen, without any of the characteristic blue colour of a carbonic oxide flame. Indeed, anyone may try for himself the instructive experiment of gradually adding hydrogen to a carbonic oxide flame burning in air and noting the point at which its characteristic blue colour vanishes. The evidence of our eyes, unaided by the spectroscope, tells us (*a*) that the radiation emitted by a carbonic oxide flame is very different in quality from that of a hydrogen flame, and

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* *Proc. Roy. Soc.* A. **109** (1925), pp. 177–186 and 523–4.

(*b*) that somehow or other the gradual addition of hydrogen rapidly diminishes, and finally almost obliterates, the difference.

As long ago as 1890, complete analyses of the infra-red radiation from different flames was made by W. H. Julius in Berlin, who reported * that in all flames producing both carbon dioxide and steam most of the radiation was concentrated into two bands, the wave lengths of which are respectively $4{\cdot}4\mu$ and $2{\cdot}8\mu$. He also found that with a pure H_2-flame the $4{\cdot}4\mu$ band disappeared, the other remaining, whilst with a pure CO-flame the $2{\cdot}8\mu$ band is absent. About the same time R. von Helmholtz by means of a bolometer measured the radiation (per litre of gas burned) emitted by flames of given size, finding about 2·4 times as much from a pure CO-flame as from a pure H_2-flame.

Moreover, quite apart from visual evidence or scientific tests, it has long been recognised among practical steel-makers that, *ceteris paribus*, carbonic oxide is a better open hearth furnace fuel than hydrogen ; thus they are wont to contrast the good ‘ soaking ’ heat given in these furnaces by a CO-rich ‘ producer gas ’ with the ‘ cutting ’ heat given by a ‘ producer gas ’ in which the proportions of hydrogen and carbonic oxide are reversed. It is possible that, even if well-founded, such an idea has little connection with the mechanism of combustion of the two gases ; on the other hand, it may be of some significance.

It has been long known that the flame of carbonic oxide gives a continuous spectrum extending from the visible into the ultra-violet region, quite distinct from the ‘ oxy-carbon ’ spectrum yielded by the oxides of carbon under the influence of an electric discharge. Also, as far back as 1886, Burch had observed that when carbonic oxide is burned under reduced pressure the flame spectrum shews signs of becoming discontinuous † with ill-defined maxima of light in positions not incompatible with the supposition that they might be vestiges of the ‘ oxy-carbon ’ bands. Dr. F. R. Weston’s investigations have dispelled such suppositions and greatly added to our knowledge of the subject.

F. R. Weston’s Experiments

Highly purified carbonic oxide, and hydrogen quite free from hydrocarbon impurity, were used in his experiments, for which a Bellingham and Stanley quartz spectrograph, having a wave-length range from approximately 6000 A.U. in the visible to 2100 A.U. in the ultra-violet region, was employed. It may be recalled that the boundary line between the visible and ultra-violet region lies somewhere about 3800 A.U. Four different series of experiments were made, which will now be described in their order.

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* *Die Licht und Wärmestrahlung verbrannte Gaze*, Berlin, 1890.

† *Nature*, xxv. p. 165. See also A. Smithells, *Phil. Mag.* 1901, pp. 476 to 503.

FIRST SERIES

Spectrographic Comparison of Carbonic Oxide, Hydrogen and Water-gas Flames in Air at Atmospheric Pressure

In this series of experiments the gas or gas mixture (undried) was burnt at a plain silver jet, inserted in the end of a glass tube, the flame being placed directly in front of the slit of the spectrograph for (in each case) a period of an hour and a half, which sufficed to give a good photographic record, Imperial 'ordinary' plates being used. In the first instance, spectrograms were obtained of the flames of a range of combustible gases beginning with 100 carbonic oxide (*i.e.* pure CO), then passing successively through 92·5/7·5, 80/20, 75/25, 50/50, 27·5/72·5 CO/H_2 finally to 100 (*i.e.* pure) hydrogen. Some of these are shewn in Plate XXIV, Nos. 1 to 5, inclusive. In this way the effects of gradually replacing carbon monoxide by hydrogen in the flame were brought out.

In Nos. 1 and 5 are reproduced (*a*) the characteristic spectrogram of a pure carbonic oxide flame, and (*b*) that of a pure hydrogen flame, respectively; whilst the intermediate spectrograms (Nos. 2 to 4, inclusive) are those of flames in which carbon monoxide was progressively replaced by hydrogen, No. 4 being that of a $50CO/50H_2$ (*i.e.* 'water-gas') flame.

In the spectrogram (No. 1) of pure undried carbon monoxide can be seen, besides two groups of 'steam' lines, a banded radiation, extending from 5000 A.U. in the visible region to 2200 A.U. far in the ultra-violet, on which a continuous spectrum is superimposed. Presumably both the banded and the continuous spectra are associated with the characteristic colour and actinic properties of a carbon monoxide flame.

As the carbon monoxide in the burning gas was progressively replaced by hydrogen (Nos. 2 to 4 inclusive), both the banded and the continuous parts of the spectrum rapidly faded away, until with an equimolecular $CO\text{-}H_2$ ('water-gas') mixture they had nearly all disappeared leaving only 'steam' lines visible in the spectrogram shown in Plate XXIV, No. 4.* The intensity of these lines increased as the replacement of CO by H_2 continued, until finally they reached a maximum in the spectrum of a pure hydrogen flame (No. 5). Another noteworthy feature of this series of experiments is the rapid shortening of the extreme ultra-violet of the continuous CO-spectrum produced by the progressive additions of hydrogen to the flame; indeed, the progressive suppression of both the continuous and the banded CO-spectra by the successive H_2-additions was by no means uniform over the whole radiation, but in the first stages affected the extreme ultra-violet most of all. In Plate XXIV, Nos. 6 and 7, are

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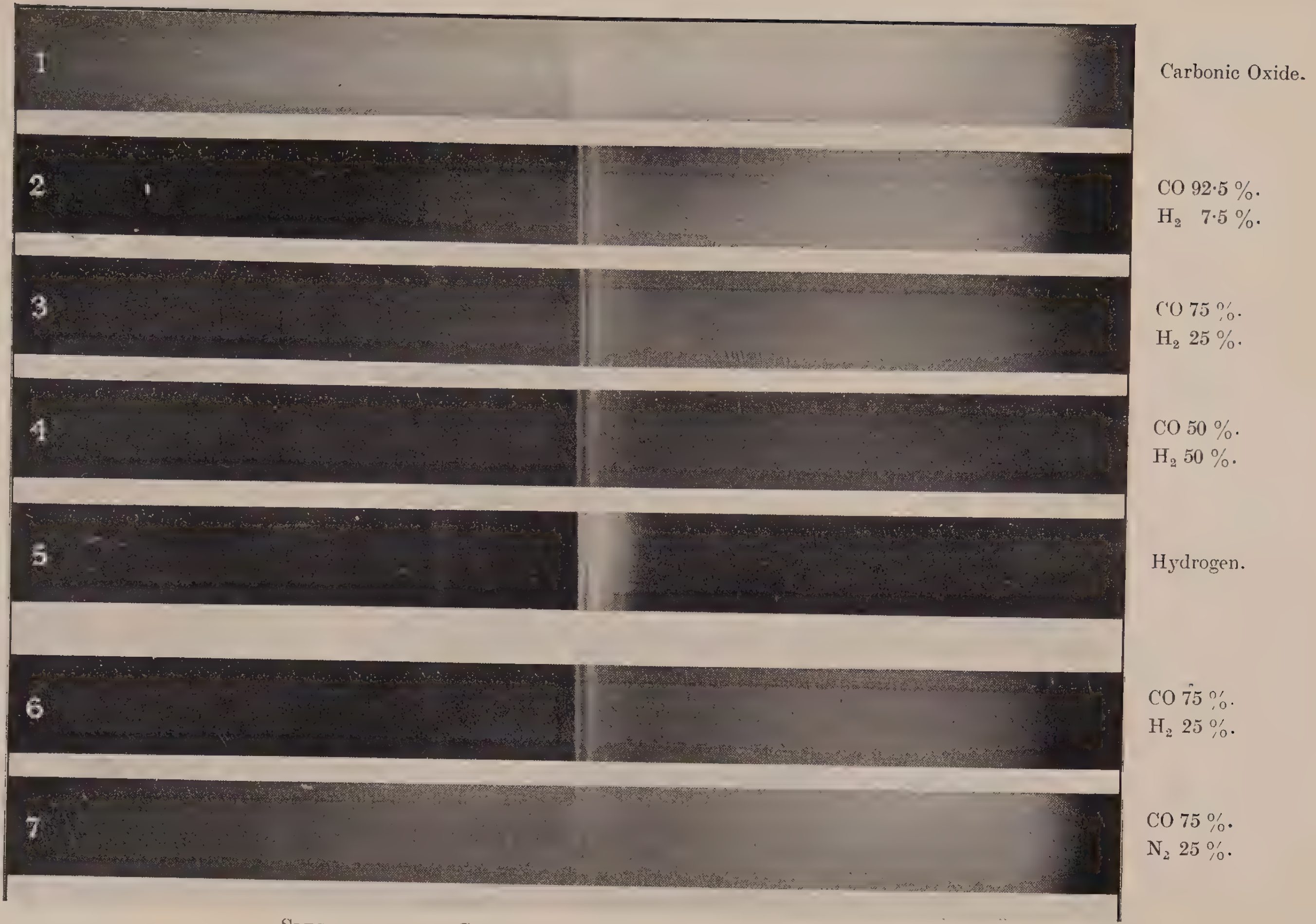
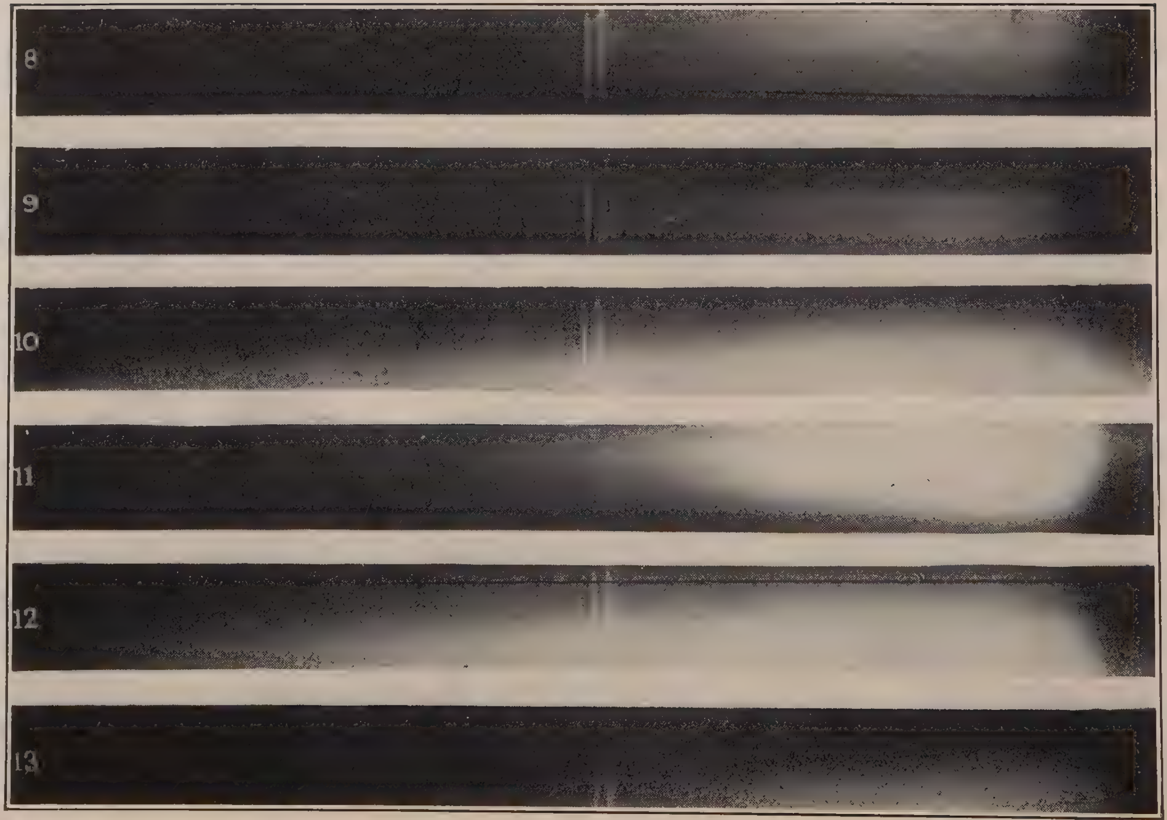
* The banded and continuous parts in the 'water-gas' spectrogram are just faintly visible in the original negative, but do not show at all in the print (Plate XXIV, No. 4) obtained from it.

PLATE XXIV.



Spectrograms of Carbonic Oxide, Hydrogen and Water Gas Flames in Air

PLATE XXV.



SPECTROGRAMS OF CARBONIC OXIDE FLAMES IN DIFFERENT ATMOSPHERES.

reproduced for comparison the spectrograms of a 75/25 $CO-H_2$ flame and a 75/25 $CO-N_2$ flame respectively, from which it can be seen (and it is still more clearly brought out in the original negative) that the effect upon the continuous and the banded CO-spectra of the addition of hydrogen is something more than a mere 'diluent' one; because, as compared with the spectrogram of a 75/25 $CO-N_2$ flame, that of the 75/25 $CO-H_2$ flame shews the continuous and banded CO-spectra to be decidedly fainter and at both ends more foreshortened.

It may here be recalled that the flame of 'blue' water gas, which usually contains about 40 to 43 per cent. of carbon monoxide and between 45 and 50 per cent. of hydrogen, has much the same appearance as a hydrogen flame, having none of the characteristic colour of a CO flame about it; the reason for this now becomes evident, for, as spectrograph No. 5 shews, in such a flame the particular radiation which gives rise to the characteristic colour of a pure CO flame would be practically all suppressed, leaving that corresponding with the 'steam-lines' of a hydrogen flame.

SECOND SERIES

Spectra of Carbonic Oxide Flames in Different Atmospheres

The spectrograms of pure (undried) carbon-monoxide flames burning in various supporting atmospheres were next compared. For this purpose a jet of pure moist carbon-monoxide was burnt at the upper enlarged opening (4 mm.) of a 1 mm. bore silica tube *A* (see Fig. 135), fixed in the vertical axis of the cylindrical glass enclosure *B*, *B*, which was fitted with quartz side windows *C*, *C*; a side-tube *D* for the admission of the supporter of combustion; a glass chimney *E*, communicating with an exit-tube *F*, to which (if need be) a large pressure-equalizing vessel, manometer, and suction pump could be attached in series. In this way a carbon-monoxide flame could be maintained in any desired atmosphere and at any pressure, from 1 atmosphere downwards to about 50 mm. In taking the spectrograms, the radiation from the flame, after passing through the quartz window, was focussed by means of a quartz lens upon the slit of the spectrograph. The times of exposure were from 45 to 60 minutes, panchromatic plates being used.

In Plate XXV (Nos. 8 to 13, inclusive) are shewn some of the spectrograms obtained from CO flames burning at atmospheric pressure in various supporting media, such as ordinary air (No. 8), argon-air (*i.e.*

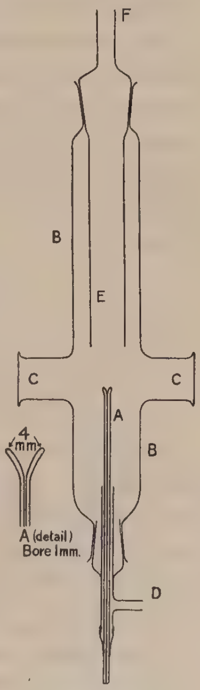


FIG. 135.

O_2+4Ar, No. 9), undried oxygen (No. 10), well-dried oxygen * (No. 11), 6 per cent. ozonised oxygen (No. 12), and nitrous oxide (No. 13). There was no material difference between those (Nos. 8 and 9) obtained when the supporting atmosphere was either ordinary air or argon-air, respectively. When, however, it was *undried* oxygen (No. 10), the continuous part of the CO spectrum was much intensified, and prolonged much farther into the ultra-violet. With well-dried oxygen (No. 11) the intensity of the continuous part of the CO spectrum remained undiminished, but the 'steam lines' had become very faint indeed.* The general character of the CO-oxygen spectrum was not much affected by ozonizing the oxygen (No. 12), although, if anything, it became more distinctly banded towards the extreme ultra-violet end. Finally, the spectrogram obtained with nitrous oxide (No. 13) was much less intense than with oxygen as the supporting atmosphere and resembled more the CO-air spectrogram.

THIRD SERIES

Spectra of Carbonic Oxide Flames in Oxygen at Different Pressures

In Plate XXVI (Nos. 14 to 16, inclusive) are shewn three of a series of spectrograms obtained when pure (undried) CO flames were maintained in atmospheres of undried oxygen at progressively diminishing pressures between 765 and 61 mm.

The chief interest of this series lies in the fact that, as the pressure was progressively reduced, the banded part of the CO spectrum became more distinct, and the continuous part became less intense. Diminution of the pressure, however, did not seem to affect the positions of the bands but only made them more distinct as the intensity of the continuous spectrum diminished. The 'steam-lines' were invariably present in all the spectrograms.

FOURTH SERIES

Spectra of Hydrogen, Carbonic Oxide and Water-Gas Flames in Oxygen-rich Atmospheres

In these experiments the flames in question were maintained in an oxygen-rich atmosphere immediately in front of the slit of the spectrograph without any quartz window or the like intervening, whereby, as the result of the much better illumination of the slit, more intensive spectrograms were obtained.

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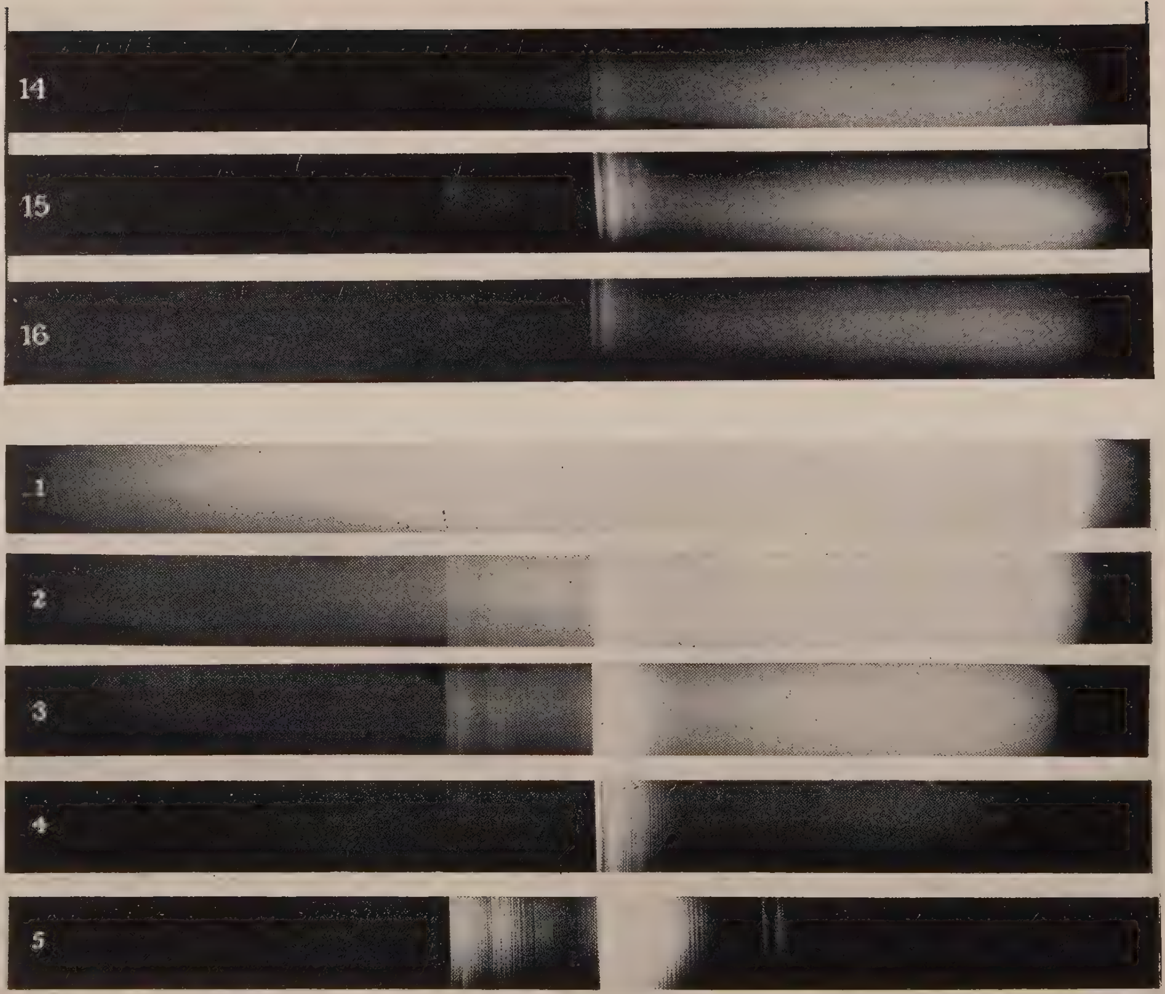
* In this experiment, both the CO and the oxygen were dried by passage through concentrated sulphuric acid ; in such circumstances it was more difficult than with the undried gases to maintain a continuous flame indefinitely, and it was usually necessary to re-kindle it three or four times during an experiment extending over two hours.

PLATE XXVI.



THIRD SERIES.

CO in O_2.

	Pressure.	Exposure.
14	765 mm.	60 mins.
15	100 mm.	90 mins.
16	61 mm.	150 mins.

FOURTH SERIES.

1 Carbonic Oxide.

2 CO 88 %. H_2 12 %.

3 CO 78 %. H_2 22 %.

4 CO 53 %. H_2 47 %.

5 Hydrogen.

The procedure adopted in these experiments will be understood by reference to the accompanying diagram (Fig. 136). A jet of the combustible gas was ignited as it issued from the expanded orifice *A* of the 1-mm. bore quartz tube *BB*. This orifice had been previously expanded in the oxy-hydrogen blowpipe until it had acquired the particular form shewn in the diagram. The quartz tube was suitably mounted co-axially with a wider glass tube *CC* (internal diameter 8 mm.), having a side-arm *D*, through which a stream of oxygen was maintained. The flame at the orifice *A* was thus surrounded by an atmosphere of oxygen; and by placing the burner at a distance of about 1 cm. from the slit *S* of the Bellingham and Stanley spectrograph (wave-length range 6000 A.U. to 2100 A.U.), much more intensive spectrograms were obtained for oxy-carbon monoxide and oxy-hydrogen flames than by the method previously employed. In each case the undried combustible gas, stored over a mixture of equal volumes of glycerine and water, was burnt at a constant rate of 10 litres per hour; and a 45 minutes exposure was allowed in taking the spectrograms, Imperial 'ordinary' plates being used.

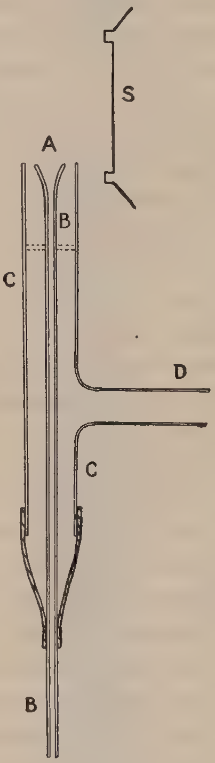


FIG. 136.

A selection of the spectrograms so obtained is shewn in the accompanying Plate XXVI: in making these reproductions from the original negatives the exposures used were in all cases the same, viz. 20 seconds, in an enlarging lantern with a 60-watt lamp as the illuminant.

No. 1, which was obtained from a flame of pure (undried) carbon monoxide, shews a very strong continuous spectrum extending far into the ultra-violet (certainly up to 2200 A.U.), its intensity being such that the characteristic CO-bands in the region 5500 to 3900 A.U. observed in previous experiments were now completely masked. On the other hand, the broad bands which had been previously noticed in the region 2800 to 2300 A.U. of the spectrogram of a CO-'ozonised'-oxygen flame were now brought out rather more distinctly. The intensity of this CO-oxygen continuous spectrum almost masked the CO-OH_2 'steam lines,' which were now only faintly visible. No. 5 is the spectrogram obtained from a flame of pure undried hydrogen burning in an envelope of oxygen; the normal 'steam lines' are shown much intensified.

In Nos. 2 to 4, inclusive, are shewn in a very striking way the effects of gradually adding hydrogen to the burning gas until the equimolecular 'water-gas' mixture is reached. It will be seen that in confirmation of previous results (*q.v.*) such addition of hydrogen immediately caused a marked and rapid diminution both in the range and intensity of the continuous CO-oxygen spectrum, until, with the 'water-gas' equimolecular mixture (No. 4), it had practically all disappeared leaving only the CO-OH_2 steam lines visible in the print. It should, however, be stated that in the original negative vestiges of the continuous CO-oxygen spectrum can be seen in the region 4300 to 3300 A.U., though in the print they are hardly visible at all.

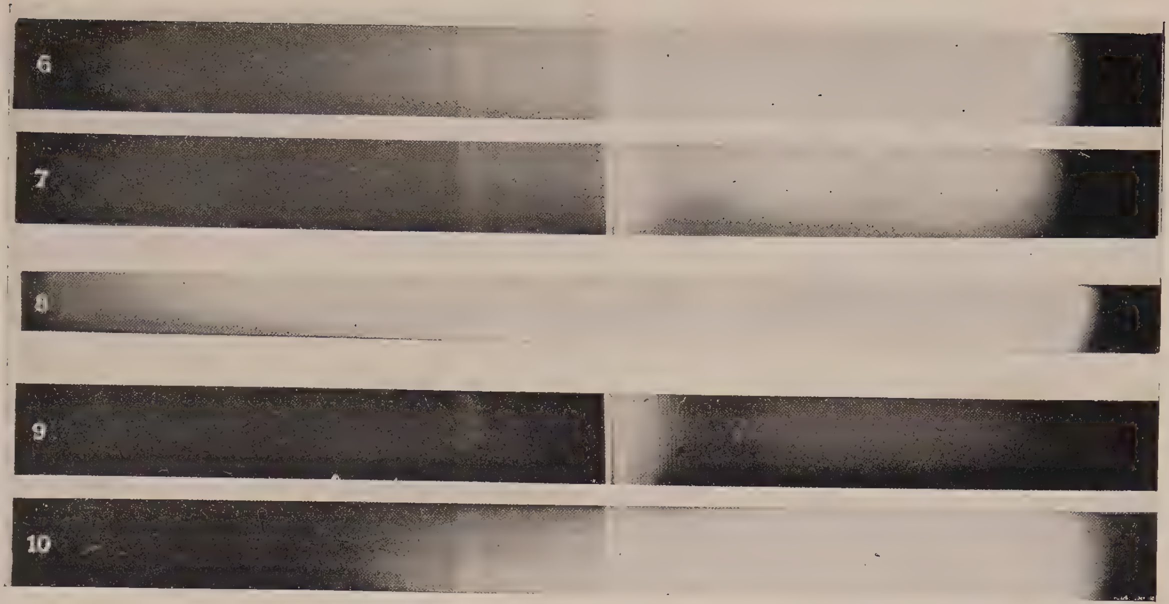
In order to ascertain whether the addition of a certain volumetric proportion of steam to the burning carbon monoxide would have any appreciably different effect upon the flame spectrum from that produced by the addition of the same volumetric proportion of hydrogen, spectrograms of the flame of carbon monoxide saturated with steam in the one case at 50° and the other at 75° C., respectively, were next taken, the barometric pressure being about 763 mm. in each case. The gas burnt would thus contain in the one case about 12 per cent. and in the other about 38 per cent. of steam respectively. On subsequently comparing the spectrogram (No. 6, Plate XXVII) obtained by burning CO containing 12 per cent. of steam with that (No. 2) obtained by burning CO containing 12 per cent. of hydrogen, no material difference between them could be detected. On the other hand, the addition of 38 per cent. of steam (No. 7, Plate XXVII) seemed to have little more effect than the addition of only 22 per cent. of hydrogen (No. 3).

That the observed effects upon the continuous and banded parts of the CO-flame spectrum of adding either hydrogen or steam to the burning gas were not due to a mere physical adsorption of such radiation by steam was proved in the next experiment in which a hydrogen flame was interposed between the pure CO flame and the slit of the spectrograph, so that the radiation emitted by the burning carbon monoxide had to pass through the hydrogen flame before entering the spectrograph. No difference, however, could be detected between the resulting spectrograph (No. 8) and that (No. 1) obtained when the same CO flame was burnt without any interposition of a hydrogen flame between it and the slit of the spectrograph. This shews that a hydrogen flame is quite transparent to that part of the radiation from a CO flame which produces the characteristic continuous part of its spectrum.

In Nos. 9 and 10 (Plate XXVII) are reproduced the spectrograms obtained from flames of equimolecular mixtures of CO and H_2 and of CO and N_2 respectively. Exactly the same volume of CO was burnt in the 45 minutes duration of each of the two experiments, but it was diluted in the one case with its own volume of hydrogen and in the other with nitrogen, otherwise the conditions were all the same. The unmistakable difference here shewn between the two spectrograms in question proves that the suppression by hydrogen (and/or steam) of the continuous part of the CO-flame spectrum in the case of the 'water-gas' flame is no mere

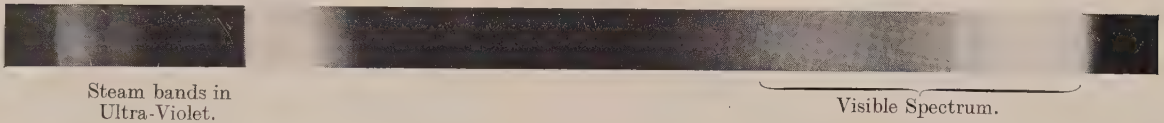
PLATE XXVII.

FOURTH SERIES (*Cont.*).



SPECTROGRAMS OF CARBONIC OXIDE FLAMES SHOWING INFLUENCE OF STEAM, ETC.

No. 11.



FLAME SPECTRUM OF H_2 WITH ADDITION OF N_2O BURNING IN AIR. (Dixon and Higgins.)

diluent effect. Presumably, therefore, it is due to the supersession of the CO-oxygen by the CO-steam interactions in the flame.

Prof. A. Fowler's Description of the Carbonic Oxide Flame Spectrum

Professor A. Fowler, F.R.S., whose eminence as a spectroscopist is universally recognised, examined all the CO-flame spectrograms obtained by Dr. Weston during the research, and furnished the following description of them :

"The spectrum of the flame of carbonic oxide burning in air appears to consist of a continuous spectrum of considerable intensity upon which is superposed an ill-defined band spectrum. The ultra-violet bands of water vapour are also a conspicuous feature.

TABLE A.—BAND SPECTRUM OF THE CARBON MONOXIDE FLAME

Wave-length.	Intensity.	Wave-number.	Wave-length.	Intensity.	Wave-number.
5555	0	18,002	4528	2	22,085
5490	0	18,210	4485	2	22,297
5430	2	18,416	4437	1	22,538
5392	1	18,546	4413	2	22,669
5348	1	18,699	4367	1	22,899
5318	2	18,804	4344	2	23,020
5278	3	18,947	4335	1	23,068
5226	1	19,135	4307	0	23,218
5169	3	19,346	4298	1	23,267
5129	3	19,497	4260	2	23,474
5082	0	19,677	4235	1	23,613
5026	2	19,897	4203	1	23,793
4981	2	20,076	4154	2	24,073
4932	2	20,276	4141	1	24,149
4896	3	20,425	4130	1	24,213
4851	1	20,614	4104	1	24,366
4817	1	20,760	4093	1	24,432
4798	2	20,842	4073	1	24,552
4769	2	20,969	4063	1	24,612
4724	1	21,169	4045	1	24,722
4659	2	21,464	4034	1	24,789
4654	2	21,487	4008	1	24,950
4608	1	21,701	4000	1	25,000
4598	1	21,782	3966	0	25,214
4577	2	21,848	3942	1	25,368
4557	2	21,944	3911	2	25,569

"Measurements of the flame bands have been made on a photograph taken with a Hilger quartz spectrograph (size E. 2), giving a dispersion of 110 A. per mm. at 5900 and 20 A. per mm. at 3100. It was not found possible to measure the bands under a microscope, and the method adopted was to superpose an ivory scale, divided to hundredths of an inch, on the negative. A comparison spectrum of iron furnished the necessary standards. The resulting wave-lengths are subject to probable errors of at least 2 or 3 Angstrom units. The wave-lengths of the bands which appear in the less refrangible part of the spectrum are included in Table A, p. 331. The intensities tabulated in the second column are rough estimates, on a scale of 3 for the brightest bands, ranging through 2 and 1 for fainter bands to 0 for bands which are just easily perceptible on the negative. Wave numbers, in air, corresponding to the tabulated wave-lengths, are indicated in the third column of the table. The bands continue far beyond the limit of the table, but until some method of producing them with better definition has been found it scarcely seems worth while to tabulate them, especially as the more refrangible part of the spectrum is complicated by the presence of the bands of water vapour.

TABLE B.—STRUCTURE OF THE BAND SPECTRUM OF THE CARBON MONOXIDE FLAME

18,416(2)	*531*	18,947(3)	*550*	19,497(3)		
388		*399*		*400*		
18,804(2)	*542*	19,346(3)	*551*	19,897(2)		
				379		
				20,276(2)	*566*	20,842(2)
20,076(2)	*538*	20,614(1)	*555*	21,169(1)		
349		*355*				
20,425(3)	*544*	20,969(2)				
335						
20,760(1)						
				21,944(2)	*594*	22,538(1)
				353		*361*
		21,701(1)	*596*	22,297(2)	*602*	22,899(1)
		384		*372*		*368*
21,487(2)	*598*	22,085(2)	*584*	22,669(2)	*598*	23,267(1)
				351		*346*
				23,020(2)	*593*	23,613(1)
						24,612(1)
						338
23,218(0)	*575*	23,793(1)	*573*	24,366(1)	*584*	24,950(1)
		356		*356*		
		24,149(1)	*573*	24,722(1)		
23,474(2)	*599*	24,073(2)				
		359				
		24,432(1)	*568*	25,000(1)	*569*	25,569(2)
				368		
				25,368(1)		

"Regularity in the distribution of many of the bands seems sufficiently evident on inspection of the negative, but on account of the approximate character of the wave-numbers it is somewhat difficult to establish the regularity numerically. The partial analysis of the spectrum, however, making due allowance for probable errors of the wave-numbers, will serve to indicate that the bands are in all probability distributed in accordance with the general laws which govern the structure of band spectra (see Table B, p. 332).

"It will be observed that the differences in the columns and rows are as nearly equal as is to be expected from the rough measures at present available, and that the differences are of the same order of magnitude in different parts of the spectrum. It seems clear that the CO flame bands constitute a characteristic spectrum which is quite distinct from the more familiar 'oxy-carbon' bands which have been observed in vacuum tubes."

Interpretation of the Results

The outstanding facts disclosed by Dr. Weston's experiments may be summarised as follows:

(1) The flame spectrum of pure *undried* carbonic oxide burning in air or oxygen at atmospheric pressure consists of three distinct parts, namely: (*a*) a strong continuous spectrum extending from about 5500 A.U. in the visible certainly up to 2200 A.U., and possibly even farther, in the ultra-violet region, and for the most part superposed upon (*b*) an ill-defined band spectrum, and (*c*) the characteristic ultra-violet bands of water vapour (the 'steam lines' or bands) and especially a prominent group in the region 3200 to 3060 A.U. Both (*a*) and (*b*) are associated with the characteristic colour and actinic properties of the flame.

(2) Enrichment of the supporting atmosphere by oxygen much intensifies the continuous part (*a*) of the spectrum; also, *drying* the gases (*i.e.* the carbonic oxide and the oxygen) by means of strong sulphuric acid before combustion almost obliterates the 'steam lines' without diminishing the intensity of the continuous spectrum.

(3) A progressive reduction in pressure causes the banded part (*b*) of the spectrum to become more distinct, although the diminution in pressure does not seem to affect the position of the bands, which are also quite distinct from the more familiar 'oxy-carbon' bands frequently observed in vacuum tubes.

(4) The gradual addition of hydrogen to a carbonic oxide flame causes the banded and continuous parts of the spectrum rapidly to disappear until with an equimolecular (water-gas) mixture only vestiges of them remain, leaving only 'steam lines' recognisable.* The addition of

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* Vestiges of the continuous and banded parts are just faintly visible in the original spectrogram—negative of a 'water-gas' flame, but usually do not shew at all in the prints therefrom.

steam to the burning gas has much the same effect as hydrogen, though on the whole less marked.

(5) A hydrogen flame is quite transparent to that part of the radiation from a CO-flame which produces the characteristic continuous part of its spectrum.

It should also here be stated that, subsequent to the publication of Dr. Weston's second paper, Bone and Newitt shewed that when a *well-dried* CO-air mixture ($2CO + 1\frac{1}{8}O_2 + 4\frac{1}{2}N_2$) is exploded in a cylindrical steel bomb (*previously well dried out*) fitted with a quartz window, the resulting flame spectrogram shews a continuous and diffused band spectrum extending up to 2780 A.U. in the ultra-violet without any 'steam lines' being discernible, (see Plate XXVIII in our next chapter, where further details of the experiments will be given).

It seems difficult, if not impossible, to explain the foregoing facts except on the supposition that carbonic oxide burns in two different ways, which ordinarily occur simultaneously, namely, (1) in which steam does not function chemically, in the sense of being continuously decomposed and regenerated, and (2) in which it does so function.

Indeed we think the experimental evidence set forth in this and the next chapter naturally leads to the conclusion that in a flame of pure (undried) carbonic oxide two sets of independent interactions occur simultaneously, namely: (*a*) direct interactions between carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded parts of the spectrum, and to the characteristic blue colour of the flame, and (*b*) interactions between CO and OH_2 molecules, which originate the 'steam lines' in the spectrum. When hydrogen (or steam) is gradually added to the burning gas the relative proportions of the first named interactions diminish rather rapidly, and proportionately more of the CO is burnt by interaction with OH_2 molecules; finally, when an equimolecular (water-gas) mixture of carbonic oxide and hydrogen is burnt, the CO-steam interactions occur to the practical exclusion of the CO-oxygen interactions. The importance of Dr. Weston's spectrographic work in regard to the mechanism of CO-combustion lies in the fact that it has afforded what H. B. Dixon has described as "the first clear evidence that in an ordinary CO-flame both the direct and indirect actions are going on at once."

Perhaps the most remarkable feature about the CO-flame spectrum is the fact that it is for the most part a continuous one, because hitherto it has been generally supposed that a gas, or reacting gases, cannot give a continuous spectrum. The flame certainly contains no *solid* particles. Possibly what has been called the 'continuous' part of the CO-flame spectrum is really a 'banded' spectrum much diffused; and the fact that a reduction in pressure increases the distinctiveness of the bands may be held by some to support such supposition. Usually, however, band spectra are regarded as in a separate category from continuous spectra of the black body type, although possibly they may become continuous under sufficient pressure. This aspect of the matter needs further investigation before any definite conclusion can be reached. Meanwhile, it may be mentioned that H. B. Dixon and W. H. Higgins * recently reported having observed that the introduction of nitrous oxide into a hydrogen flame burning in air causes it to increase in size and become luminous ; also, that the jet of issuing gas is surrounded by a luminous apricot-coloured zone, whose spectrum develops a seemingly continuous portion from red to violet in the visible region, in addition to the usual 'steam lines' in the ultra-violet (as shewn in Plate XXVII, No. 11). Therefore, it seems as though the usual view that reacting gases cannot give rise to a continuous spectrum may have to be revised.

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* Private communication ; also Report in *Nature* for 16th December, 1926, of a paper read at the Manchester Literary and Philosophical Society, 2nd November, 1926.

CHAPTER XXVII

THE COMBUSTION OF CARBONIC OXIDE (*Continued*)—OLD THEORIES CONSIDERED IN THE LIGHT OF NEW EXPERIMENTS

Theories as to the Function of Steam

In this chapter we prefer to consider how the various theories advanced from time to time during the past forty years to explain the influence of steam upon the combustion of carbonic oxide appear in the light of recent experimental developments.

For some years after H. B. Dixon's discovery that thoroughly drying a mixture of carbonic oxide and oxygen by prolonged contact with phosphoric anhydride renders it non-explosive when a spark of moderate intensity is passed through it, purely chemical explanations, introducing the idea that steam molecules act as 'carriers of oxygen' to the combustible gas, were most in favour. Thus Dixon supposed that, in the ordinary combustion of carbonic oxide, the steam acts catalytically, as follows:

$$\text{(i) } CO + OH_2 = CO_2 + H_2,$$

$$\text{(ii) } 2H_2 + O_2 = 2H_2O, \text{ etc.}$$

In other words, it was then supposed that, carbonic oxide and oxygen being *ex hypothesi* mutually inert in flames, steam is necessary to the combustion, acting as a 'carrier of oxygen,' itself being continuously decomposed and regenerated during the process. Sometimes the idea was expressed in a different way, namely, that carbon dioxide, being so readily dissociated at high temperatures, would have difficulty in being born in flames as the result of direct encounters between CO and O_2 molecules, which are strongly exothermic, but would easily arise as the result of the much 'cooler' interactions between carbonic oxide and steam. In other words, it was supposed that steam, being much less dissociated than carbon dioxide in flames, can be produced so much more easily in them by *direct* oxidation; also that being highly reactive towards carbonic oxide at such temperatures, it naturally acts as a carrier of oxygen to it, enabling the resulting carbon dioxide to be born in a relatively much cooler and less agitated condition than otherwise it would be. Hence, it was thought that the function of steam is to bring molecules of carbon dioxide into existence with a much less degree of internal agitation, and therefore more capable of continued existence, than would be possible otherwise. Thus in his Bakerian Lecture upon "The Rate of Explosion of Gases" (1893), Dixon said, "*at the extreme temperature of the explosion wave, as well as in ordinary combustion, carbonic oxide is oxidised by steam and not directly by oxygen,*"* although three years later he modified this view as the result of his own experiments upon the explosion of cyanogen (see Chapter XXIV, p. 309-310).

Moritz Traube (in 1882) † and Mendeléeff (in 1891) put forward a modification of Dixon's view, postulating the intermediate formation of hydrogen peroxide during the combustion of carbon monoxide. In his *Principles of Chemistry* (1891 Edition), Mendeléeff ascribed the supposed mutual inertness of carbon monoxide and oxygen to the operation of a supposed 'law of equal volumes,' whereby in all cases of flames and gaseous explosions the *primary* change involves the collision of two molecules only. In the case of carbonic oxide he postulated the following cycle of dimolecular interactions :

$$\begin{array}{ll} \text{(i)} & CO + OH_2 = CO_2 + H_2, \\ \text{(ii)} & H_2 + O_2 = H_2O_2, \\ \text{(iii)} & H_2O_2 + CO = CO_2 + H_2O. \end{array}$$

The force of such an argument was, however, considerably weakened when Dixon was able to shew that well-dried mixtures of carbonic oxide and nitrous oxide, or of carbonic oxide and ozone, are just as difficult to explode as a well-dried $2CO + O_2$ mixture.

H. E. Armstrong, who always contends that chemical interactions cannot occur between two perfectly pure substances, but require an electrolyte to form a 'closed conducting circuit,' supposed that the presence of steam, which he regards as being rendered conducting by association with some traces of an electrolyte impurity, provides the necessary conditions for the passage of the current, the oxygen playing the part of depolariser,‡ as follows :

$$\begin{array}{c|c|c} \multicolumn{3}{c}{\textit{Before.}} \\ CO & OH_2 & O \\ CO & OH_2 & O \end{array} \qquad \begin{array}{c|c} \multicolumn{2}{c}{\textit{After.}} \\ CO_2 & H_2O \\ CO_2 & H_2O \end{array}$$

According to this view, the molecules of oxygen and a combustible gas are in all circumstances absolutely inert towards each other. Indeed, quite recently Armstrong declared carbon monoxide to be "*per se* an incombustible gas," adding that "*an explanation may be found in the assumption that when a moist carbon monoxide mixture is sparked or fired, some hydrone is decomposed and sufficient hydrogen set free to act in a 'depolarising' circuit together with the oxide, as thus*": *

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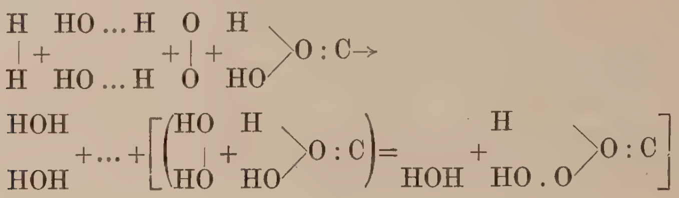
* *Phil. Trans.* A. (1893), p. 112.

† *Berichte,* 15 (1882), p. 666.

‡ *Trans. Chem. Soc.* 49 (1886), p. 112.



$$=2H_2O+CO_2.$$

This is perhaps the most elaborate and extreme form which any chemical explanation has hitherto taken, although all of them involve the assumption that in the combustion of carbonic oxide steam is continuously decomposed and regenerated.

The extreme view maintained by H. E. Armstrong ignores that there are several well-established cases (*e.g.* those of cyanogen, carbon disulphide and hydrocarbons) in which apparently combustion does not depend upon the presence of moisture. Moreover, any chemical view postulating that carbonic oxide cannot be burnt in flames except by the intervention of steam, which is continuously decomposed and regenerated in the process, is countered by the spectroscopic evidence discussed in our previous chapter. Indeed, even without recourse to the spectroscope, our eyes tell us that the visible radiation from a carbonic oxide flame is different in quality from that emitted by a hydrogen flame, from which it follows that the intensive reactions which originate the visible radiation in each case cannot be the same, as they would be if carbonic oxide is always *indirectly* burnt by interaction with steam, and never by *direct* interaction with oxygen, in flames.

It may here be remarked that, whilst it cannot be seriously contended that CO and OH_2 molecules are incapable of interacting in flames—for no one familiar with the subject would deny that they ordinarily do so in such circumstances—it is a very different matter to assert, as some have done, that in no circumstances can carbonic oxide be burnt except through the chemical intervention of steam in some such way as we have indicated. Indeed, the real issue nowadays is not whether, or how, the presence of a minute quantity of steam may assist, or be conducive to, the combustion of carbonic oxide—a fact which no one can deny—but whether or not the presence of some steam is *essential* to the process.

Whilst, up to the present, the chemical theories referred to have well-nigh monopolised attention, there have never been wanting alternative physical explanations worthy of consideration. For example, as far back as 1886,

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* *Proc. Roy. Soc.* B. **98** (1925), pp. 202–206.

Lothar Meyer was led by his experiments (see Chapter XXIV, p. 309) to put forward the view that a far higher temperature is required to initiate the interaction between carbonic oxide and oxygen than between carbonic oxide and steam ; so that, whereas the latter is easily initiated by a spark of low intensity, the former requires one of high intensity.

Later on the observations of Dixon, in conjunction with Strange and Graham, upon the explosion of a well-dried mixture of cyanogen with twice its own volume of oxygen, as well as those of Smithells and Dent upon a cyanogen flame, which have already been dealt with in Chapter XVII (*q.v.*) suggested that when carbonic oxide is freshly formed in a flame, and therefore in an 'ionised' condition, it will combine directly with oxygen, as indeed Dixon himself admitted.

In 1893 J. J. Thomson pointed out that if the forces holding the atoms together in a molecule are, as we now believe, electrical in character, the presence of drops of any liquid, such as water, of high specific inductive capacity would probably cause a sufficient loosening of the bonds between the atom to render the molecule much more reactive. For, he said: "If we take the view that the forces which hold the atom in the molecule together are electrical in their origin, it is evident that these forces will be very much diminished when the molecule is close to the surface of or surrounded by a conductor or a substance like water possessing a very large specific inductive capacity." He also shewed that the complete drying of a gas renders it non-conductive even when subjected to considerable electrical potentials.* In 1910 he again reminded chemists that combustion is concerned not only with atoms and molecules but also with electrons.†

H. B. Baker, in his Wilde Lecture before the Manchester Literary and Philosophical Society in 1909, described a number of new experiments which led him to conclude that "ionisation without water is ineffective in producing chemical action"; ‡ and he tentatively suggested that chemical interchange in gaseous systems depends upon the presence of both 'ions' and water vapour; thus the 'ions' act as nuclei for the condensation of steam, and the liquid drops of water so formed, by virtue of their high specific inductive capacity, facilitate chemical change in the layer of gas immediately in contact with them.

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* *Phil. Mag.* 36 (1893), p. 321.

† *Brit. Assoc. Reports* (Sheffield), 1920, p. 33.

‡ *Man. Mem.* 53 (1909), pp. 1 to 8.

SOME NEW EXPERIMENTS (1923–5)

(1) *Effect of Progressive ‘ Drying ’ upon the Minimum Condenser Discharge required to Ignite a Mixture of Carbonic Oxide and Oxygen at Atmospheric Pressure*

In the course of the researches carried out at the Imperial College, London, by the authors in conjunction with Dr. D. M. Newitt upon gaseous combustion at high initial pressures, it was discovered that the presence of water vapour has very little influence upon the rate of pressure development in the explosion of a theoretical CO-air mixture

$$(2CO + O_2 + 3{\cdot}76N_2)$$

at an initial pressure of 50 atmospheres, as the following results indicate :

TABLE LXXXIX.—INFLUENCE OF MOISTURE ON THE EXPLOSION OF A $2CO + O_2 + 3{\cdot}76N_2$ MIXTURE AT AN INITIAL PRESSURE OF 50 ATMOSPHERES (BONE, NEWITT AND TOWNEND)

Hygroscopic State of the Gases and Explosion Chamber.	Time Taken for Attainment of Maximum Pressure. Sec.	Maximum Pressure Developed. Atmos.	Per cent. Pressure Fall in 0·5 Sec. After P_m.
(1) P_2O_5—dried -	0·18	400	9·0
(2) Undried -	0·15	411	10·0
(3) Moist - -	0·19	395	11·5

These results suggested to us, and independently to H. B. Dixon also, that, supposing (as we believed) the ‘ dryness ’ of the bomb system in our Series I. experiments could be relied upon, carbonic oxide combines directly with oxygen at high pressures without the intervention of steam.

So much did this conviction grow upon us that when F. R. Weston joined our research group in 1923 he was asked to undertake, as his share of the work, an experimental re-examination of the whole subject. This he did in a research extending over the next three years, the results of which, together with those of other cognate experiments made by R. P. Fraser and D. M. Newitt, were published in the *Proceedings of the Royal Society.**

The first series of experiments which Dr. Weston took up were designed to determine how the ignitibility of a mixture of carbonic oxide and oxygen in combining proportions is affected by progressively drying it. H. B. Dixon had shewn that a P_2O_5-dried mixture would not ignite when electric sparks of comparatively moderate intensity are passed through it ; but, in view of W. M. Thornton’s later discovery that, for given sparking conditions (*e.g.* electrodes, type of discharge, voltage, etc.), a certain 'minimum spark energy' is required to ignite a given explosive mixture, it seemed possible that Dixon's sparks had been too feeble to ignite his well-dried mixture, and that even the driest possible mixture might be exploded if sparks of sufficient intensity are used. Thornton had studied (*inter alia*) the igniting powers of condenser-discharge sparks, which are oscillatory and of extremely short duration, and start with ionisation of the gas between the poles; and he proved that "there is in every case a well-marked limit to their igniting power." Thus, in the case of an undried CO-air mixture containing 20 per cent. of the combustible gas, he found that with a 100-volt condenser discharge a minimum capacity of 2 microfarads was required for ignition.

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* *Proc. Roy. Soc.* A. 110 (1926), pp. 615 to 645.

It seemed that if the presence of water vapour has any material influence upon the ignitibility of a given explosive mixture of carbon monoxide and oxygen (say, $2CO + O_2$), then the minimum condenser discharge spark-energy required to ignite it ought to vary according to the amount of water vapour present; so that, on progressively drying such a mixture from a condition of (say) 'saturation' at room temperature to one which is in equilibrium with a fairly efficient drying agent, as, for example, freshly-ignited calcium chloride, the minimum spark-energy required for ignition should progressively increase until at length it becomes many times greater than ordinarily it is.

On putting the matter to the test of experiment this anticipation proved to be correct, the minimum spark energy required to ignite a calcium-chloride-dried $2CO + O_2$ mixture being some thirty times greater than for the same mixture when saturated with water vapour at the room temperature.

The experimental procedure consisted in determining the minimum condenser discharge spark-energy required to ignite a mixture of highly purified carbonic oxide and oxygen, in varying hygroscopic states, contained in a special glass explosion vessel (similar to the one shown in Fig. 139) which was fitted with stout platinum electrodes. A number of condensers of known capacity, which had been previously calibrated by means of a ballistic galvanometer and a 1 microfarad standard condenser, were charged from the mains up to 110 volts, as verified by an electrostatic voltmeter. The condensers were connected up with the electrodes of the explosion vessel through a double-pole double-throw switch; and by gently tilting the explosion vessel the gap between the electrodes was reduced until the condenser discharged across it.

To begin with, a capacity was used well below that required to ignite the particular mixture under investigation, and a trial was made. The capacity was then gradually increased, in steps of 0·1 or 0·25 microfarad, until a point was reached at which the mixture was fired by the discharge spark. Three trials were given at each successive capacity before increasing it; and whenever several trials were necessary before reaching the 'limiting' capacity, a special redetermination of the latter was made. Every precaution was taken to keep the electrodes perfectly clean throughout a given series of experiments; indeed, the whole elaborate cleaning operation described in the original Royal Society paper being repeated after every three or four ignitions. The results obtained were as follows:

TABLE XC.—INFLUENCE OF HYGROSCOPIC CONDITION OF A $2CO + O_2$ MIXTURE ON MINIMUM IGNITING SPARK CAPACITY (BONE AND WESTON)

	Hygroscopic Condition of $2CO + O_2$ Mixture.		Minimum Igniting Capacity at 110 Volts Microfarads.	Energy of Minimum Igniting Spark. $\Sigma = \frac{1}{2} cv^2$ Joules $\times 10^6$.
	Saturated with Aqueous Vapour at °C.	Per cent. H_2O by Volume Present.		
Mixture 'saturated' at room temperature	17·4°	2·00	0·76	4,600
	17·0°	1·98		
	14·5°	1·70	0·83	5,020
	14·0°	1·60	0·98	5,930
Mixture 'saturated' at a low temperature controlled by ice or some freezing mixture	4·0°	0·80	4·00	24,200
	0·0°	0·60	4·80	29,040
	− 5·0°	0·40	8·00	48,400
	−10·0°	0·26	10·07	60,900
	−16·0°	0·16	17·25	104,350
	−25·0°	0·06	18·79	113,800
Mixture	$CaCl_2$ dried	0·03	20·83	126,000

The results, which are plotted on the graph shown in Fig. 137, are all seen to fall very near to a smooth curve. They prove that as the water vapour is progressively removed from a $2CO + O_2$ mixture its ignitibility by condenser discharge sparks rapidly diminishes, the minimum spark energy necessary to fire it increasing until with a calcium chloride-dried mixture it becomes something between twenty and thirty fold as great as that required to ignite the same mixture when 'saturated' with moisture at the room temperature (14° to 17·5° C.).

It is known that the discharge of a condenser, by bringing together wires attached to its terminals, is characterized by extreme rapidity, the first oscillation being completed in less than a millionth of a second. Its effects are certainly 'impulsive'; the spark starts with collision-ionization of the gas between the poles, which rises to a maximum in the first oscillation. Presumably it also has a high temperature, and gives rise to high local gas pressure, as is evident from the sharp crackling sound emitted. As the result of recent (unpublished) experiments, however, it has been demonstrated that the 'compression wave' set up in the gaseous mixture when the discharge is passed plays no part in the ignition, which presumably is due to 'ionization' of the gases by the spark. So that the foregoing experiments would seem to prove that the progressive drying of a mixture of carbonic oxide and oxygen necessitates an increasingly powerful 'ionizing' spark for its ignition.

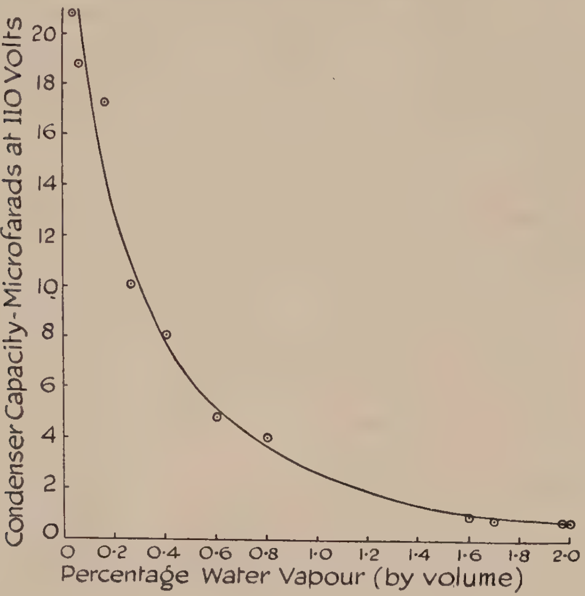


Fig. 137.

(2) *Proof that a Rigidly-Dried Mixture of Carbonic Oxide and Oxygen can be Exploded at Atmospheric Pressure by a Sufficiently Powerful Condenser Discharge.*

The next step in the experimental inquiry was to ascertain whether or not an explosive $2CO + O_2$ mixture which had been rigidly dried by prolonged exposure to phosphoric anhydride can be exploded by a sufficiently powerful condenser discharge. For this purpose, it was necessary to adopt special precautions in order to ensure, not only the utmost cleanliness in the explosion vessels used, but also the most efficient drying possible of the gaseous mixture and its absolute freedom from all impurities.

This involved a very elaborate experimental ritual, the details of which are fully described in the Royal Society paper (*loc. cit.*). The apparatus employed for the preparation and purification of the gases, their admixture in the desired proportions, and the preliminary drying by means of redistilled phosphoric anhydride and liquid air, is shown in Fig. 138. It was constructed in one piece throughout, all joints in it being of fused glass; all the five stopcocks included in it were lubricated with syrupy phosphoric acid, because it was absolutely necessary to avoid the use of any organic lubricant.

The experimental mixture of the two gases in their combining proportions ($2CO + O_2$) having been made in the graduated glass burette *F* over dry redistilled mercury, it was subsequently transferred to each of four glass explosion vessels *L* in the following manner: The whole of the apparatus to the right of *F* was, first of all, thoroughly exhausted down to 0·01 mm. through the tap *d* by means of a Hyvac pump, which was kept continuously running for at least twenty-four hours, and in some cases for three or four days. During this period the explosion vessel was several times strongly heated externally with a naked Bunsen flame to ensure the removal, as far as possible, of any moisture film still adhering to its walls. The platinum electrodes were also electrically 'glowed out' *in vacuo* for about eight hours in order to remove from them any occluded hydrogen, etc. Finally, the tap *d* having been closed, the gaseous mixture was very slowly passed, at a rate between 0·5 and 1 c.c. per minute, from the gas burette *F*, through the drying system to the right thereof, into the explosion vessel *L*. This drying system comprised (i) a glass spiral *G* immersed in a bath of liquid air, and (ii) two tubes *H* and *K*, altogether 100 cm. long, filled with pure redistilled phosphoric anhydride. Also, a quantity of similarly purified phosphoric anhydride had been previously introduced into the lower part of the explosion vessel *L* through its side tube *e*. As soon as the manometer *M*, which was connected with the system through the P_2O_5-filled guard-tube *N*, indicated that the explosion vessel *L* was full of the gaseous mixture at a pressure of about 10 mm. below the barometric at the time, a blowpipe flame was applied at the constriction θ, previously made in the glass capillary leading into the explosion vessel, and its contents sealed off in the usual manner.

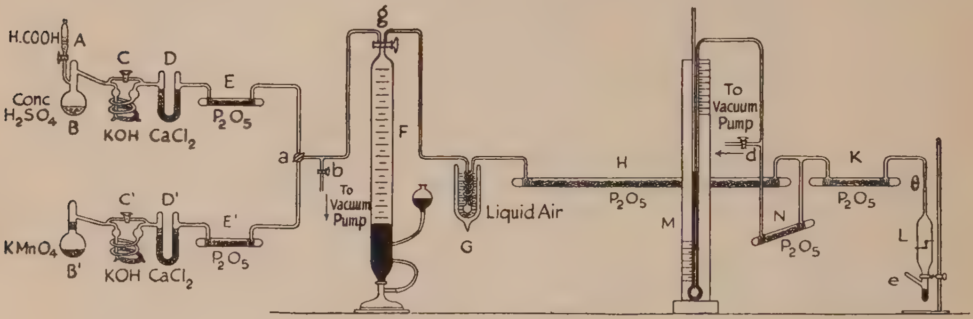


FIG. 138.

Four such explosion vessels (see Fig. 139), each of about 100 c.c. capacity and containing pure redistilled phosphoric anhydride in their lower limbs, having thus been filled with the liquid-air- and P_2O_5-dried $2CO + O_2$ mixture at the room temperature and a pressure of about 740 mm., each was put aside in a dark place for a period of six months, in order to ensure as complete a drying as possible of the gaseous mixture in contact with the phosphoric anhydride. During this ‘ drying period ’ the lower limb of each vessel was frequently tapped in order to expose a fresh P_2O_5 surface to the gaseous mixture. Also, once every fortnight, all parts of each vessel down to the side tube were externally heated to about 175° C. by means of a specially designed electric heater, in order to disperse and get rid of any ‘ moisture-film ’ adhering to the inner walls, care being taken to screen the P_2O_5 in the lower limb from the effects of the heating.

The Explosion of the Rigidly-dried $2CO + O_2$ *Mixtures.* Altogether, four bulbs containing P_2O_5-dried $2CO + O_2$ mixtures were prepared in the manner just described, and after a six-months' drying period their ignitibilities by the said condenser discharge were tested. The general result was that, whereas ignition could not be effected with a condenser capacity of 0·5 microfarad, *i.e.* with a ‘ spark energy ’ of less than about 0·235 Joule, at the aforesaid voltage, it always occurred instantly, and at first shot, with a condenser capacity of 0·77 microfarad or more, *i.e.* a spark energy of 0·362 Joule, or more.

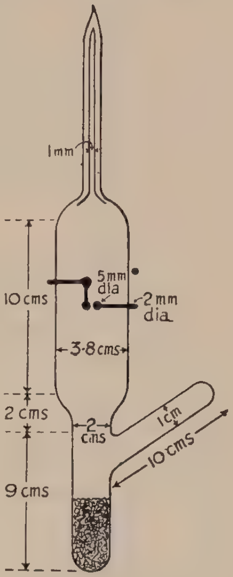


FIG. 139.

Some idea of how powerful a spark was needed to ignite the mixtures may be gathered from the estimate of Captain Finch, who was in charge of the firing arrangements, that in the circuit employed the peak current of the first oscillation of the discharge spark from a 0·75 microfarad condenser at 970 volts would be certainly not less than 700 amperes, and possibly many times more. Moreover, it should be stated that when the discharge from a 0·5 microfarad condenser failed to ignite the mixtures, the spark simply passed across the gap between the electrodes without any sign whatever of a ‘ halo ’ or such-like appearance.

In all four cases, with a spark energy of 0·362 *Joule or more, the mixture was instantly ignited at first shot, the resulting explosion spreading with a brilliant flame fairly rapidly through the containing vessel.* Judging, however, from sound and appearance, the explosions never seemed to be quite so ‘ sharp ’ as they were in similar bulbs with an ‘ undried ’ or even a ‘ $CaCl_2$-dried ’ $2CO + O_2$ mixture ; and the combustion was never, in fact, quite complete, there always being a small residue of uncombined combustible mixture.

The explosion of No. 1 mixture was effected at first shot with a ‘ spark energy ’ of 0·47 Joule (1 microfarad at 970 volts) after two previous failures, at several hours intervals, with ‘ spark energies ’ of 0·052 and 0·235 Joule (0·11 and 0·5 microfarad at 970 volts, respectively). The flame spread throughout the mixture more rapidly than the eye could follow, the powdery phosphoric anhydride in the lower part of the vessel being violently thrown up by the explosion, some of it as high as the electrodes. Subsequent analysis of the products showed that the combustion had been 77·2 per cent. complete.

The explosion of No. 2 mixture, which was effected at first shot with a ‘spark energy’ of 0·94 Joule (2 microfarads at 970 volts), was witnessed by Profs. H. E. Armstrong and A. Smithells, Sir Robert Robertson and others; that of No. 3 mixture was carried out in the presence of Prof. H. B. Baker at first shot with a ‘spark energy’ of 2·35 Joules. In each of these cases a brilliant flame quickly filled the vessel, and subsequent analysis of the products showed the combustion to have been about 88 per cent. complete.

The explosion of No. 4 mixture was effected at first shot with a ‘spark energy’ of 0·362 Joule (0·75 microfarad at 970 volts), after a previous failure three days before with a ‘spark energy’ of 0·235 Joule only (0·5 microfarad at 970 volts). The flame spread rapidly throughout the mixture, and a photograph of the explosion (which is reproduced in Plate XXVIII, Fig. 140), shewed that it had completely filled the vessel. Subsequent analysis of the products shewed the combustion to have been about 74·3 per cent. complete. Full particulars of these experiments are set out in Table XCI.

It would thus appear that the minimum condenser ‘spark energy,’ at 970 volts, required to ignite such P_2O_5-dried mixtures as the foregoing probably lies somewhere between 0·235 and 0·362 Joule. It is also evident that, at such extreme dryness, even when the ‘spark energy’ was sufficient to ignite the gaseous mixture, and the resulting flame spread rapidly throughout it, its resistance to combustion was still so great that an appreciable amount of it remained unburnt. Thus it was always noticed that the explosions were comparatively ‘soft’ ones, no ‘click’ being audible in any of them; and the incompleteness of the combustions indicated a ‘reluctance to burn,’ as though the flame was rather deficient in self-igniting power.

Attention is directed to the fact that in the four experiments under consideration, the greater the energy (up to a limit) of the spark which ignited the mixture, the more complete was the combustion in the subsequent explosion, thus:

Energy of the Spark Causing Ignition. Joule.	Per cent. Combustion.
0·362	74·3
0·47	77·2
0·94 2·35	88·0 approx.

Table XCI.—Showing Results of Experiments upon the Explosion of the P_2O_5-dried $2CO + O_2$ Mixtures (Bone and Weston).

No. of Experiment.	Percentage Composition of the Gaseous Mixture.			Explosion Vessel Filled at :	Drying Period Weeks.	Details of Firing Trials.	Final Pressure (corrd.) of Cold Products mm.	Ratio P_2/P_1.	Percentage Composition of the Gaseous Products.				Per cent. CO Burnt.
	CO.	O_2.	N_2.	°C. and mm.					CO_2.	CO.	O_2.	N_2.	
1	65·9	33·4	0·7	18·5° 744·2	25	(i) With 0·11 microfarad at 97 0volts. Σ=0·052 Joule. *No ignition.* (ii) With 0·50 microfarad at 970 volts. Σ=0·235 Joule. *No ignition.* (iii) With 1·0 microfarad at 970 volts. Σ=0·47 Joule. *Instant Explosion.*	544·0	0·73	66·7	19·8	11·8	1·7	77·2
2	65·6	33·4	1·0	17·0° 738·7	27	With 2·0 microfarads at 970 volts. Σ=0·94 Joule. *Instant Explosion.*	527·0	0·715	81·5	11·1	5·5	1·9	88·0
3	65·8	33·5	0·7	16·5° 741·0	31	With 5·0 microfarads at 970 volts. Σ=2·35 Joules. *Instant Explosion.*	526·0	0·71	80·8	11·7	5·9	1·6	87·5
4	66·2	33·0	0·8	19·0° 733·5	24	(i) With 0·5 microfarad at 970 volts. Σ=0·235 Joule. *No ignition.* (ii) With 0·77 microfarad at 970 volts. Σ=0·362 Joule. *Instant Explosion.*	551·5	0·75	64·0	22·2	11·8	2·0	74·3

In this connection it may be mentioned also that in some similar comparative experiments where the $2CO+O_2$ mixtures had been dried for one or two weeks in contact with well-ignited calcium chloride, the minimum condenser spark discharge energy required for ignition seemed to be somewhere between 0·052 and 0·235 Joule (0·11 and 0·5 microfarad, respectively, at 970 volts). The resulting explosions were certainly sharper (a distinct 'click' being usually audible) and the combustions more complete than was the case in the corresponding experiments with the P_2O_5-dried mixtures.

Such results suggest that, for a given degree of dryness of the mixture, the greater the ionizing impulse imparted to it by the igniting spark, the more complete is the resulting combustion as the flame spreads through the explosive mixture ; but this point is reserved for further investigation. Meanwhile, it may be concluded from this section of the research :

(1) that as water vapour is progressively removed from a $2CO+O_2$ mixture, its 'ignitibility' by condenser discharge sparks rapidly diminishes, the 'minimum spark energy' necessary to fire it increasing until, with a calcium chloride-dried mixture, it becomes something like twenty or thirtyfold as great as that required to fire the same mixture when saturated with moisture at a temperature of 15° C. ;

(2) that a $2CO+O_2$ mixture which has been dried to an extreme degree by prolonged (six months) contact with pure phosphoric anhydride can still be ignited and exploded, provided that a spark of sufficient energy be passed through it, though the gases display a much greater 'resistance' to combination than when even a minute amount of moisture is present ; and

(3) that there is some property of the electric spark, presumably its ionizing power, which, if only developed strongly enough, can overcome the high resistance of such an extremely dry mixture to ignition and explosion, and by virtue of which it can, so to speak, compensate the system for the absence of water vapour.

(3) *Experiments Showing the Influence of Pressure upon the Ignitibility of a Rigidly-Dried* $2CO+O_2$ *Mixture*

While Dr. Weston was engaged upon the experiments just described, Mr. R. P. Fraser was carrying out another series with the object of elucidating the influence of pressure upon the ignitibility by electric sparks of a rigidly-dried mixture of carbonic oxide and oxygen in their combining proportions. It was shown that, with a spark across a 1/100 inch gap from a 1-inch Marconi induction coil, with a current at 6 volts in the primary circuit, a rigidly-dried and highly-purified mixture of carbonic oxide and

PLATE XXVIII.

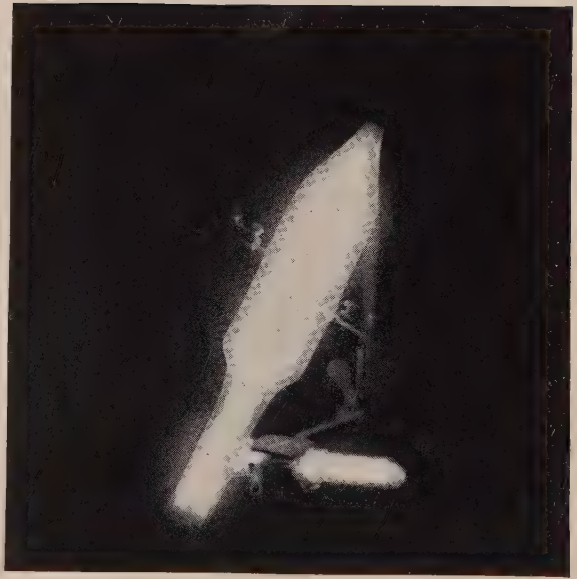
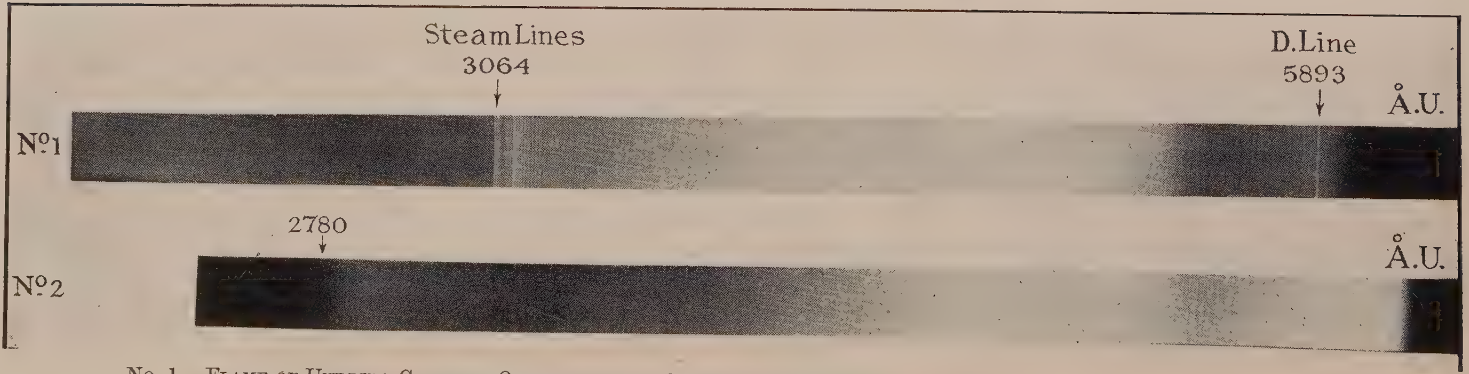


Fig. 140.



No. 1.—Flame of Undried Carbonic Oxide burnt at Ordinary Pressure in Air.

No. 2.—Explosion Flame of CO-Air ($2CO + 1\frac{1}{8}O_2 + 4\frac{1}{2}N_2$) fired at an Initial Pressure of 25 Atmospheres—the Flame oxygen could not be ignited at atmospheric pressure, no matter how many sparks were passed. On increasing its pressure to 3 atmospheres, the mixture was fired after several unsuccessful attempts, albeit the resulting combustion was only 90 per cent. complete. With an initial pressure of 5 atmospheres, or more, the mixture could always be fired at first attempt, though the resulting combustion was never complete unless the initial pressure exceeded 10 atmospheres or thereabouts, as the following experimental data show : *

TABLE XCII.—INFLUENCE OF INITIAL PRESSURE ON THE IGNITIBILITY OF A DRY $2CO+O_2$ MIXTURE (BONE AND FRASER)

Experiment.	Initial Pressure. Atmospheres.	Result.	Percentage Combustion.
With a $2CO+O_2$ mixture dried for a year in contact with re-distilled phosphoric anhydride - - 1 -	1·0	Could not be ignited	—
2 -	1·5		—
3 -	3·0	Fired after many attempts	90·1
4 -	5·0	Always fired at first attempt	93·4
5 -	10·7		99·1
6 -	19·0		99·3

It thus appears that pressure will overcome the reluctance to burn of a rigidly-dried mixture of carbonic oxide and oxygen, a result which suggested that at high initial pressures the two gases will readily combine without any chemical intervention of steam at all.

(4) *Spectrographic Evidence from Explosions of Well-Dried* CO-*Air Mixtures under Pressure*

This last-named deduction has been experimentally verified in our laboratories by Dr. D. M. Newitt in the following most conclusive manner. He exploded a well-dried CO-air mixture, of composition $2CO+1\frac{1}{8}O_2+4\frac{1}{2}N_2$, at an initial pressure of 25 atmospheres, in a cylindrical steel bomb (previously well dried-out) fitted at each end with a quartz window, and, by means of a Hilger No. E2 quartz spectrograph placed in position outside one end of the explosion chamber, he took a photo-spectrogram of the resulting explosion flame advancing in a direction towards the slit of the spectrograph. This spectrogram (Plate XXVIII, No. 2) shewed a continuous and diffused band-spectrum extending up to 2780 A.U. in the ultra-violet without any 'steam lines' being discernible. Above it is reproduced, for comparison, a spectrogram (No. 1) obtained in a preliminary experiment with the same Hilger E2 instrument, of the flame of *undried* carbon monoxide burning at a jet in air at atmospheric pressure, the same amount of the gas being so burnt as was subsequently exploded in the bomb. It will be observed that, while the spectrogram (No. 1) of the *undried* CO-flame at atmospheric pressure extended up to 2200 A.U. in the ultra-violet, and shewed unmistakably the 'steam lines,' in the region 3060 A.U. due to radiations excited by CO and OH_2 interactions, as well as the continuous and diffused band-spectrum, due to radiation excited by *direct* CO and O_2 interactions, the corresponding spectrogram (No. 2) of the explosion flame of the well-dried CO-air mixture burning in the bomb under pressure is foreshortened in the ultra-violet and exhibits no 'steam lines' at all, a result of the highest significance.

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* For details of the experimental procedure, and particularly of the 'drying' operation, the original paper (*Proc. Roy. Soc.* A. 110, pp. 634 to 645), should be consulted ; it also contains details of Dr. Newitt's experiments) which will be referred to in the paragraphs under (4).

(5) *Further Photographic Experiments*

After completing the foregoing experiments Dr. Weston commenced a further investigation with a view to gaining information as to the mode and speed of propagation of flame through a rigidly P_2O_5-dried $2CO_2+O_2$ mixture. For this purpose the mixture, prepared and dried in the manner described on pp. 343-5 (see also Fig. 138), was sealed up at atmospheric pressure over phosphoric anhyride in a horizontal glass tube (Fig. 141) 35 cms. long, fitted in the middle with platinum electrodes. The tube had previously been cleaned out and dried according to the ritual already described. After being filled with the dried gases the tube was set aside for 60 days to ensure a thorough drying-out of the system. Finally, its contents were ignited by a discharge from a condenser of 3·75 microfarads capacity charged up to 1000 volts, and as the resulting flame moved horizontally towards each end of the tube it was photographed on a film moving vertically at a known speed. At the same time, for comparative purposes, a 'control' experiment was made on precisely similar lines but with a *moist* $2CO+O_2$ mixture, all conditions other than the 'drying' being alike in the two experiments.

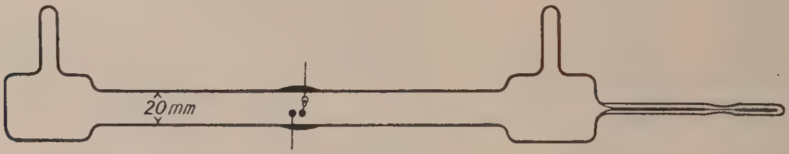
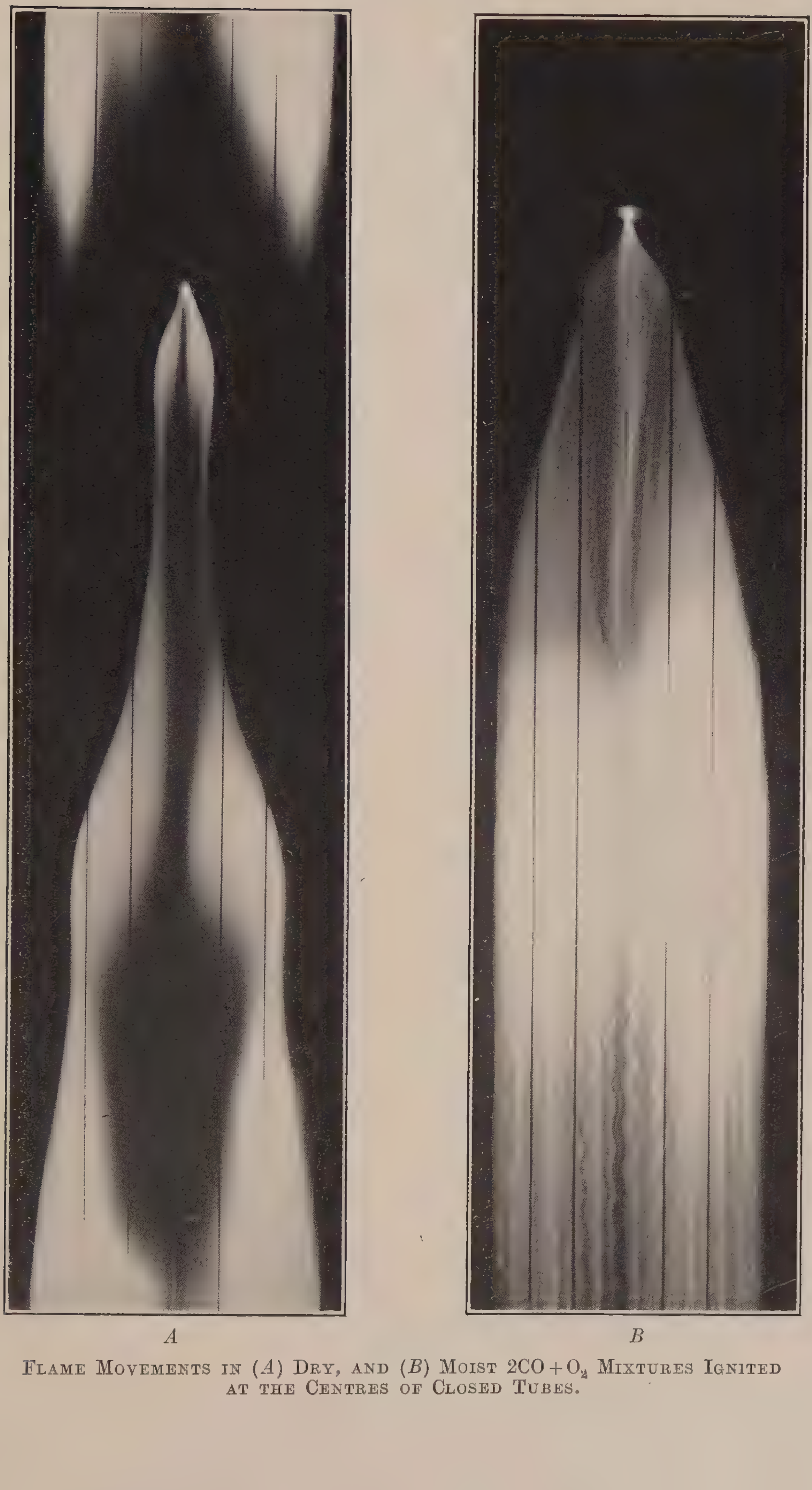


FIG. 141.

The resulting photographs are shewn side by side in Plate XXIX, *A* being the 'dry' and *B* the 'moist' explosion flame. It will be observed that in both cases ignition occurred at the instant of the discharge. In the case of *A*, however, the initial flame speed was only about one-tenth that in *B* (the speed of the film in *B* being $12\frac{1}{2}$ times that in *A*); after

PLATE XXIX.



A

B

Flame Movements in (*A*) Dry, and (*B*) Moist $2CO + O_2$ Mixtures Ignited at the Centres of Closed Tubes.

travelling about 2·5 cms. in each direction along the tube the flame fronts in *A* became almost stationary for a period, then moving forward again nearly to the closed ends of the tube, with however another almost stationary period. Finally the main combustion set in when each flame front had nearly reached the closed end, and at the instant the whole tube was nearly filled with a brilliant flame, the combustion being 91 per cent. complete. This picture should be contrasted with *B*, where the flame-fronts moved continually forward at much greater speeds than in *A*, although here again there was a sudden burst of luminosity when the flames reached the closed ends of the tube, combustion being now 100 per cent. complete.

Concluding Remarks

In view of the fundamental importance of the subject we feel that no apology is needed for having devoted so many pages to its discussion. And although its investigation is being continued, and will go on perhaps indefinitely—for there is no finality about it—it may be claimed that definite progress has been made, and a new point of view established, as the result of the experiments described in this chapter. We will, therefore, conclude by summarising what we consider this to be.

In the first place, we think that the new facts which up to now have emerged from the inquiry have proved beyond any reasonable doubt that *the presence of steam is not essential to the ignition and explosion of* carbonic oxide and oxygen mixtures, as has been supposed hitherto, but that the two gases can and do combine directly without its intervention.

Secondly, the spectrographic evidence shews undoubtedly that when *undried* carbon monoxide is burnt at a jet in undried air (or oxygen) at ordinary pressures, both the *direct* and *indirect* oxidations go on simultaneously and independently ; also, that it is the radiations excited by the *direct* CO-oxygen interactions in the flame which give rise to the continuous and banded parts of its spectrum, whilst the ‘ steam lines ’ are due to radiations excited by the CO-OH_2 interactions.

Thirdly, it has been proved that an increasingly high pressure undoubtedly favours the *direct* oxidation, so that at high initial pressures it predominates to the exclusion of the *indirect* ; on the other hand, the presence of hydrogen in the burning mixture undoubtedly favours the *indirect* oxidation, so that in a water-gas flame at ordinary pressure the indirect predominates to the practical exclusion of the direct, and the character of the radiation emitted is modified accordingly, a most important consideration in its bearing upon the practical uses of water-gas and other mixtures of carbonic oxide and hydrogen. Indeed, it may now be said that the characteristic radiation emitted by a flame, in which the combustible gas is carbonic oxide only, is rapidly eliminated when hydrogen is added to the burning gas ; because, as the hydrogen content thereof increases, the more are the *direct* CO-oxygen interactions superseded by the *indirect* CO-OH_2 oxidations, until, when a 'water-gas' composition is reached, such supersession is practically complete, with the result that, so far as the character of the radiation emitted from it is concerned, a 'water-gas' flame is, to all practical intents and purposes, a 'hydrogen' flame.

Also, it should be mentioned that spectroscopic evidence obtained in other experiments shews that it is the radiation excited by the CO-oxygen interactions in the flame, giving rise to the continuous and banded parts of the spectrum, which in the explosion of CO-air mixtures under high initial pressures activates the nitrogen. On the other hand, there is also much evidence that the radiations excited by the CO-OH_2 interactions do not activate the nitrogen.

Such, in brief, is the new evidence which must be taken into account in revising our theories upon the subject. We must, however, beware of allowing our conclusions to outrun the facts; for, although we may set aside the idea that the presence of steam is in all circumstances *essential* to the combustion of carbonic oxide, much more remains to be learned before anyone would be justified in putting forward any new theory as a proven one. Therefore we will restrict ourselves to suggestions which seem to arise out of the new results, leaving the future to prove what measure of truth (if any) they may contain. For we must be guided by facts, wherever they may lead, and beware of allowing prepossessions to obscure our vision of them.

Meanwhile, many considerations make us think that the true explanation may ultimately be found in the supposition of some degree of ionisation of one (or both) of the reacting gases being a necessary precedent to their combustion. From such point of view a neutral carbonic oxide molecule may be regarded as incapable of combining with oxygen; it must somehow be 'activated,' maybe 'ionised' in some degree, before it can do so. Several agencies, including the ultra-violet radiation emitted by CO-O_2 interactions in the flame, as well as other known ionising influences, singly or in combination, may bring about the needed 'activation.' Indeed, some recent (as yet unpublished) experiments in our laboratories have afforded evidence, not only of carbonic oxide absorbing the radiation emitted by its own combustion, but also of there being a definite 'induction' period when a $2CO_2 + O_2$ mixture is ignited by a weak electric spark. This being so, then steam, besides acting chemically, as it undoubtedly does when present in sufficient concentration, may promote ionisation, even when present in much smaller proportions, by virtue of its high specific inductive capacity; or, possibly also, by condensing upon free negative electrons, it may hinder their recombination with positive ions, and so prolong and maintain the 'reactivity' of the system, which otherwise would be shorter-lived.

Another view of the matter has recently been suggested by W. E. Garner and C. H. Johnson, as the result of their experiments upon the infra-red spectrum of carbonic oxide burning in oxygen.* It was found that small quantities of water vapour depressed the infra-red radiation from the explosion, whilst at the same time they increased the rate of reaction. It is therefore suggested that the reduction in the intensity of the infra-red emission, brought about by the addition of water, is due to collision of water vapour with freshly-formed CO_2 molecules. In the absence of water, the CO_2 molecules give up their excess of internal energy as infra-red radiation, whilst in the presence of water they lose part or the whole of it by collision. In the latter case, it is supposed that the greater amount of energy thereby retained in the system caused an increase in the rate of reaction.

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* *Phil. Mag.* [vii.] 3 (1927), pp. 97-110.

CHAPTER XXVIII

THE COMBUSTION OF HYDROCARBONS. THE DOCTRINE OF PREFERENTIAL COMBUSTION

Notwithstanding the experiments of John Dalton on the partial combustion of methane and ethylene in the years 1803–4, and of Kersten on the explosion of a mixture of ethylene and electrolytic gas in the year 1861 (see Chapters III and VI, pp. 20 to 22 and 43), throughout the greater part of last century it was generally accepted as an article of faith amongst chemists that the hydrogen, being (as was supposed) so much the more combustible of the elements of a hydrocarbon, is preferentially burnt when there is defect of oxygen.

How such a doctrine first arose is not quite clear. Sometimes it has been attributed to Sir Humphry Davy, presumably because of a passage in one of his papers about the separation of carbon in a hydrocarbon flame being due to " the decomposition of a part of the gas towards the interior of the flame where the air was in smallest quantity " ; but, although the sentence in question may be somewhat ambiguous, it does not say that the hydrogen of a hydrocarbon is burnt preferentially to the carbon when the oxygen supply is deficient, but only that the gas decomposes liberating carbon in such circumstances. Possibly Davy's meaning was misunderstood by his contemporaries, for the doctrine in question arose during his lifetime and soon became firmly rooted. It was certainly countenanced by Faraday who, in his lectures at the Royal Institution on " The Chemistry of a Candle " (1848–9 and repeated in 1860–1) said : " The volatile matter raised by combustion from the tallow of a candle is a vapour composed of carbon and hydrogen . . . the forces which hold these elements together are so nicely balanced that the hydrogen is made to combine first, the carbon afterwards."

It is difficult now to see what experimental proof or basis there ever could have been for such a doctrine; it was contradicted both by Dalton's experiments and those of Kersten (*q.v.*) ; but it swayed men's minds during nearly the whole of last century, proving that dogmas are by no means the monopoly of theologians. Every chemist was brought up to believe as an article of faith that the luminosity of hydrocarbon flames is due to incandescent carbon particles liberated in the interior of the flame, where the oxygen is in defect, because of the preferential combustion of the hydrogen.

As late as 1884 H. B. Dixon, in his Cantor lectures on "The Use of Coal Gas" at the Royal Society of Arts in London, speaking of the combustion of ethylene in its bearing on the luminosity of hydrocarbon flames, said: "This ethylene, when it is raised to a high temperature in contact with air, is decomposed, the hydrogen burning first and the carbon afterwards. There is a race for the oxygen of the air between the two constituents of the ethylene, and the hydrogen, being the fleeter of the two, gets to the oxygen first, and is burnt to water"; this shews the sense in which the doctrine was held a few years before its final overthrow.

In the year 1891, however, events occurred which in a short time caused it to be completely abandoned. For in that year it was rediscovered, in H. B. Dixon's laboratory in Manchester, that an equimolecular mixture of ethylene and oxygen yields on detonation almost exactly twice its own volume of carbonic oxide and hydrogen, in accordance with the empirical equation:

$$C_2H_4+O_2=2CO+2H_2.$$

In his Bakerian lecture at the Royal Society in 1893 Dixon said (with reference to the experiments in question) "I have made experiments on the rate of the explosion-wave in ethylene and in acetylene mixed with their own volume of oxygen. In both cases the main reaction is the formation of carbonic oxide and hydrogen. . . . With ethylene and oxygen the volume was almost doubled; with acetylene and oxygen the volume was increased by one-half. . . ." *

Simultaneously, also, and quite independently, Smithells and Ingle, during their researches in flame (see Chapter XVII), discovered large quantities of hydrogen and carbonic oxide in the interconal gases of hydrocarbon flames, and said: "Perhaps the most remarkable fact apparent from our analysis is that the main chemical change occurring in the inner cone consists in the combustion of the hydrocarbons to form carbon monoxide and water with smallest quantities of carbon dioxide and hydrogen," and that they have proved "the existence of such a change with definite hydrocarbons and in a perfectly direct manner." Such facts seemed to point to the carbon burning more readily than the hydrogen of hydrocarbons, which (as they said) "is not in accordance with a widely prevailing though scarcely justifiable belief." And they concluded "We may suppose that in our experiments, when the hydrocarbon first burns in the inner cone, there is a distribution of the limited supply of oxygen between the carbon, such, that either carbon monoxide and water or carbon monoxide, water, and hydrogen are first formed," † this

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* *Phil. Trans.* A. 184 (1893), p. 161.

† *Trans. Chem. Soc.* 61 (1892), pp. 212-4.

primary change being followed by the reversible ‘water-gas’ reaction. Thus, in the case of methane, the probable sequence of changes was thought to be :

$$\text{(i)}\quad CH_4+O_2=CO+H_2O+H_2,$$

and

$$\text{(ii)}\quad CO+OH_2\rightleftharpoons CO_2+H_2.$$

In the year 1892, also, B. Lean and W. A. Bone, who were then working in H. B. Dixon’s laboratory at Manchester, published an account of experiments in which ethylene had been exploded with less than its own volume of oxygen * in a leaden coil ($\frac{3}{4}$ in. internal diameter, capacity 2·1 litres), fitted near one end with a glass firing-piece, and terminated by steel taps, through one of which connection with a manometer was made. The results, whilst generally confirming Dixon’s earlier observation with the equimolecular mixture, shewed also an increasing formation of both methane and carbon as the oxygen contents of the explosive mixture was progressively diminished. Thus, for example, whereas on exploding a nearly equimolecular mixture, containing 49·4 per cent. of ethylene, 47·7 per cent. of oxygen, and 2·9 per cent. of nitrogen, at an initial pressure of 756 mm., the cooled final products were at a pressure of 1503 mm. and contained :

$CO_2=0{\cdot}35$, $CO=49{\cdot}10$, $H_2=48{\cdot}80$, $CH_4=1{\cdot}0$ and $N_2=0{\cdot}75$ per cent.

little or no carbon being deposited during the explosion, a mixture containing 56·03 per cent. of ethylene, 39·46 per cent. of oxygen, and 4·51 per cent. of nitrogen similarly gave, as cooled products, under a pressure of about 1300 mm.

$$CO_2=1{\cdot}65,\quad CO=38{\cdot}85,\quad H_2=43{\cdot}30,\quad C_2H_4=5{\cdot}53\ \text{and}\ CH_4=5{\cdot}95\ \text{per cent.},$$

besides a copious deposit of carbon.

Five years later W. A. Bone and J. C. Cain published a paper describing similar experiments on the explosion of acetylene with less than its own volume of oxygen,† in which it was shewn that the main reaction always results in the formation of carbonic oxide and hydrogen, together with some liberation of carbon—but no methane.

Thus it may be said that the doctrine of the preferential combustion of hydrogen was finally overthrown as the result of researches independently carried out during the years 1891–4 in Manchester and Leeds by Dixon, Smithells and their pupils.

In its place was revived the idea which had been originally put forward by Kersten in 1861, that in hydrocarbon combustion generally “ before any part of the hydrogen is burnt all the carbon is burnt to carbonic oxide, and the excess of oxygen (if any) divided itself between the carbonic oxide and hydrogen.” Thus, in discussing the question of how carbon separates

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* *Trans. Chem. Soc.* 61 (1892), pp. 873 to 888.

† *Ibid.* 71 (1897), pp. 26 to 41.

in the luminous region of hydrocarbon flames, Smithells said that, whereas the doctrine about the hydrogen of a hydrocarbon burning before the carbon when the supply of oxygen is limited was not borne out by any experiments of which he was aware, with the possible exception of those of Berthelot and Vieille, the experiments of Dalton, Kersten and E. von Meyer, as well as his own, "all point to exactly the opposite conclusion, namely, that the carbon burns preferentially to the hydrogen." * And, having regard to the then-known facts, such a view was reasonable, although it has since been discarded. It was, however, vigorously opposed by H. E. Armstrong, who considered it to be "unwise at present to infer that the oxidation of the hydrocarbons or the separation of carbon and also of hydrogen from them takes place in any one way."

Lean and Bone had pointed out (*loc. cit.* p. 875), "that Dalton, Kersten and others have only shewn that carbonic oxide and hydrogen are *eventually* obtained when ethylene is fired with its own volume of oxygen. Their results do not prove that carbonic oxide and hydrogen are the immediate products of the interaction of ethylene and oxygen." For, as Sir G. G. Stokes had said: "we must carefully distinguish between the changes which take place in the partial combustion of a molecule and those which are produced in neighbouring molecules as the result of the heat produced."

The position at the end of last century was that whereas the doctrine of the preferential combustion of hydrogen had collapsed under the weight of contrary evidence resulting from the Manchester and Leeds researches, that of the preferential combustion of carbon had not met with general acceptance. Another alternative, namely, that the *initial* stage of the oxidation of a hydrocarbon might conceivably involve the transient formation of an unstable 'oxygenated' molecule, which, according to circumstances would decompose more or less rapidly under the influence of heat, giving rise to simpler 'intermediate' products, had been suggested by H. E. Armstrong, but never explored experimentally. For on p. 417 of a new edition of Miller's *Organic Chemistry*, published in 1880, he had visualised such oxidation processes as primarily involving 'hydroxylation.' In our next two chapters we shall see how this idea ultimately furnished a solution of the problem.

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* *Trans. Chem. Soc.* 61 (1892), p. 223.

CHAPTER XXIX

THE SLOW COMBUSTION OF HYDROCARBONS

In the year 1898 W. A. Bone and his collaborators (R. V. Wheeler, W. E. Stockings, G. W. Andrew, H. L. Smith and J. Drugman) commenced at the Owens College, Manchester University, a systematic investigation of the subject on new lines which led to the formulation of what is known as the hydroxylation-theory of hydrocarbon combustion. Their results were embodied in a series of papers published by the Chemical Society during the years 1902-1906.* The work was afterwards completed by a series of bomb experiments at high initial pressures carried out at Leeds University in conjunction with H. Davies, H. H. Gray, H. H. Henstock, and J. B. Dawson, the results of which were published by the Royal Society in 1915.†

The experiments covered the interactions of the hydrocarbons methane, ethane, propane, butane, ethylene, propylene, butylene, and acetylene with oxygen over a wide range of conditions, namely, from 'slow combustion' at comparatively low temperatures through ordinary 'flame combustion' right up to 'detonation' and in high-pressure explosions, and it will be convenient to consider them in such order.

Up to the end of last century very little attention had been paid to the slow combustion of hydrocarbons, although it is obvious that, if unstable 'oxygenated' molecules of any kind are initially formed when such substances are burnt, the chances of detecting or isolating them at the high temperatures of flames would be small compared with what possibly might be done at temperatures below ignition. Bone and his collaborators started by investigating the interactions of hydrocarbons and oxygen at temperatures between 300° and 500° C. with results which will now be reviewed.

Experimental Methods

Two experimental methods were principally employed, namely, (i) the 'bulb method' in which hydrocarbon-oxygen mixtures of definite compositions were sealed up at 15° C. and atmospheric pressure in borosilicate glass bulbs (60 c.c. capacity), which were subsequently maintained at some constant temperature between 250° and 400° C. for definite times, after which they were opened under mercury and their contents investigated, and (ii) a ‘ circulation method ’ in which similar mixtures were continuously circulated in a closed system comprising a heated surface of porous porcelain, ‘ worms ’ containing water for the removal of soluble intermediate products, and a manometer for recording the pressure.

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* *Trans. Chem. Soc.* **81** (1902), 535; **83** (1903), 1074; **85** (1904), 693 and 1637; **87** (1905), 910 and 1232; **89** (1906), 652, 660, 939 and 1614.

† *Phil. Trans.* A. 215 (1915), pp. 275 to 318.

The Closed Bulb Method

Cylindrical Jena borosilicate glass bulbs (length about 10 cms., diameter$=3{\cdot}5$ cms. and capacity usually between 60 and 70 ccs.), terminating at each end in a long capillary tube (1 mm. bore), were employed (Fig. 142). They were first of all thoroughly cleaned out with (*a*) hot strong nitric acid, (*b*) hot distilled water, and then dried in a current of hot filtered air. A number of such clean dry bulbs were connected in series, on the one hand with a gas-holder containing the particular hydrocarbon-oxygen mixture under investigation, and on the other through a drying tube with a Sprengel pump and manometer. When nearly vacuous each bulb was strongly heated with a Bunsen burner and the exhaustion completed. As soon as the train of bulbs was cold the mixture was slowly admitted from the holder until the pressure was 2 or 3 mm. below that of the room-atmosphere ; the capillaries of each bulb were then successively drawn out and sealed off in the blow pipe.

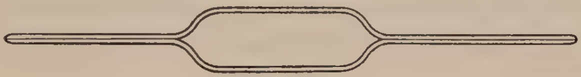

Fig. 142.

Batches of (usually) six such bulbs at a time were afterwards maintained at a definite constant temperature (usually between 300 and 350° C.), for various periods of time in a special oven the gas-supply of which was under perfect control by means of a thermostatic governor. They were then removed, quickly cooled in water, and subsequently opened *either* under mercury *or* in connection with a manometer in such a manner that the ‘ contraction in volume ’ *or* ‘ reduction in pressure ’ could be accurately measured.

The gaseous products were then drawn off by the pump for analysis, and finally each bulb was rinsed out with distilled water, and the rinsing tested for aldehydes. In analysing the gaseous products, aldehyde vapours (if present) were first of all removed (but not estimated) by keeping them for some hours in contact with sticks of zinc chloride, or the like. Other constituents were then removed and estimated by means of suitable absorbents in the following order—carbon dioxide, oxygen, unsaturated hydrocarbons (if any), and carbon monoxide. Finally, an analysis of any residual gas was made by exploding it with suitable proportions of oxygen *plus* (in special cases where such mixture was non-explosive) pure electrolytic gas. From the ratio C/A so obtained (which for methane $=2\cdot00$, ethane $=1\cdot25$) * it was ascertained whether or not the residual gas contained hydrogen and, if so, how much.

It may be pointed out that the pressure at which the original hydrocarbon and oxygen mixture would interact in such experiments would usually be somewhere between 2 and 2·2 atmospheres, according to the temperature (usually 300 to 350° C.) of the oven in which the bulbs were heated; also that the interactions occurring would always be more or less 'surface effects,' in the sense of occurring only in the layer of gas in contact with the heated walls of the bulbs. At any rate they would always start as such, and would often so continue. Consequently, in a series of experiments the observed speed with one and the same mixture at a given temperature would differ from bulb to bulb according to the different surface factor of each. Thus, for instance, it was found that, if a series of (say) ten bulbs filled with the same mixture were all maintained in the oven at the same temperature for the same time, in perhaps one or two reaction would proceed much faster, and in one or two others decidedly slower, than in the majority of them. But, by disregarding such abnormally 'fast' or 'slow' bulbs, and basing comparisons only on the 'average' result, it was usually possible to form a sufficiently approximate judgment for all practical purposes as to the 'relative reaction velocities' of different mixtures of the same hydrocarbon with oxygen.

At the outset of the research it was feared that the main course of the hydrocarbon-oxidation in such circumstances might be masked by secondary interactions between the primary products. Fortunately, however, all such fears were dispelled when it was discovered that none of the following pairs of gases shewed any sign of mutual interaction when similarly maintained in the borosilicate glass bulbs for a week at temperatures between 350° and 400° C., within which range all the hydrocarbon-oxygen mixtures examined readily reacted, namely:

(*a*) $2H_2+O_2$, (*b*) $2CO+O_2$ (moist), (*c*) $CO+H_2O \rightleftharpoons CO_2+H_2$,
(*d*) $CO+H_2$, (*e*) CH_4+H_2O, (*f*) CH_4+CO_2.

Therefore, seeing that (except in one series with methane-oxygen mixtures where 400° C. was employed) all the important hydrocarbon-oxidation experiments were carried out within the range 250 – 350° C., the primary products would not be subject to any of the foregoing secondary interactions. In other words—and this is most important to remember—in the event of either hydrogen or carbonic oxide being liberated as such during the normal oxidation process, it would not undergo any further secondary oxidation, but would remain intact until the end of the particular experiment concerned.

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* C = the contraction on explosion, and A = the absorption of CO_2 from the products by means of a strong solution of caustic potash.

Results with Methane at 350° C.

The interaction speed between this hydrocarbon and oxygen was much slower than that of any of the others examined. Thus, in the case of a mixture of the composition $2CH_4 + O_2$, which was selected for experiment because of its containing just sufficient oxygen to burn the carbon to carbonic oxide, it was hardly possible to detect any change at 300° C., unless the heating was continued over two or three weeks; at 325° C. the rate of oxidation was distinctly faster, though, in most cases, much of the original oxygen remained free after a fortnight; at 350° C., however, it had nearly all disappeared within that period. Accordingly, the results obtained with six different bulbs at 350° C. (see Table XCIII) may be taken as typical of the rest. In all cases, as soon as each bulb was removed from the oven and rapidly cooled, it was observed that (*a*) whilst no carbon had been deposited during the oxidation, a dew (which proved to be water) formed on the inner surface, and (*b*) on afterwards opening the bulb under mercury, a contraction in volume occurred corresponding with the volume of oxygen which subsequent analysis shewed had disappeared. The gaseous products always consisted of methane and the oxides of carbon, in some cases together with unchanged oxygen, but they never contained any free hydrogen.

TABLE XCIII.—RESULTS OF BULB EXPERIMENTS WITH A $2CH_4 + O_2$ MIXTURE AT 350° C. (BONE AND WHEELER)

Duration of heating in days -		1	3	7	13	13	13
Percentage composition of the N_2-free gaseous products * - -	CO_2 -	0·40	2·80	14·0	14·8	10·0	10·0
	CO -	2·15	8·95	16·3	16·0	21·5	22·2
	O -	31·40	21·80	0·9	*nil*	0·3	*nil*
	CH_4 -	66·05	66·45	68·8	69·2	68·2	67·8
Ratio CO_2/CO in products -		0·18	0·31	0·86	0·925	0·465	0·45
* Ratio C/A for residual gas exploded; proving absence of hydrogen from the products -		2·00	2·00	2·00	2·00	2·00	1·956
Other observations - - -		(i) Always steam condensed and a contraction in volume occurred. (ii) Never any carbon deposition nor hydrogen liberated.					

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* The absence of free hydrogen from these products was proved by the C/A ratio being 2·00.

Attention is specially directed to the occurrence of an always considerable CO_2/CO ratio in the products (especially at the end of the oxidation), which is a highly significant circumstance in view of the fact that the experimental conditions precluded any CO_2 formation as the result of CO-oxidation, either by means of 'moist' oxygen or through steam. Such a result indeed, quite apart from all others, necessitated some new explanation of the oxidation-process, because no then existing view would account for it.

Experiments with Ethane at 300° C.

Mixtures of ethane and oxygen were found to react quite readily at 300° C., those of the ratio either 2 : 1 or 1 : 1 doing so much faster than those containing more oxygen than the equimolecular proportion.

TABLE XCIV.—RESULTS OF BULB EXPERIMENTS WITH A $2C_2H_6+O_2$ MIXTURE AT 300° C. (BONE AND STOCKINGS)

Duration of heating		30 mins.	30 mins.	45 mins.	45 mins.
Percentage contraction		23·6	29·3	*nil*	*nil*
* Percentage composition of the N_2-free gaseous products	CO_2	3·6	6·80	1·90	2·50
	CO	15·7	28·20	36·20	35·15
	O_2	10·7	19·15	*nil*	0·20
	C_2H_6	70·0	45·85	36·50	35·45
	CH_4			10·20	10·10
	H_2			15·20	16·60
* Ratio C/A for the residual gas exploded in the analysis of the products		1·341	1·298	1·616	1·650
Other observations		(i) No carbon separated. (ii) Steam condensed on cooling. (iii) Large formation of formaldehyde and acetaldehyde, some of which vapour decomposed, producing hydrogen, methane and carbonic oxide, especially in the third and fourth experiments.			

So fast was the oxidation in such cases that usually all the original oxygen had disappeared within forty-five minutes. The process was characterised throughout by the following features : (i) no separation of carbon, (ii) an abundant aldehydic and steam formation, and (iii) (unless there was secondary aldehydic decomposition) a considerable CO_2/CO ratio. There was never any free hydrogen in the products, except when the oxidation had been fast enough to bring about the thermal decomposition of some of the formaldehyde and acetaldehyde vapours primarily formed. The results of a series of experiments with each of these fast burning mixtures are reproduced in Tables XCIV and XCV.

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* Such methane and hydrogen as was present in these products undoubtedly arose from the secondary thermal decompositions of acetaldehyde and formaldehyde vapours formed during the primary oxidation ($CH_3\cdot CHO=CH_4+CO$; $H_2:C:O=H_2+CO$), the rapid velocity of which probably raised the temperature of the reacting medium somewhat above that of its environment.

TABLE XCV.—RESULTS OF BULB EXPERIMENTS WITH AN EQUIMOLECULAR $C_2H_6+O_2$ MIXTURE AT 300° C. (BONE AND STOCKINGS)

Duration of heating - - -		45 mins.	60 mins.	10½ hrs.	23 hrs.
Percentage contraction - -		37·6	38·6	36·8	34·4
Percentage composition of the N_2-free gaseous products - -	CO_2 -	10·2	10·65	9·80	9·5
	CO -	47·7	45·30	48·25	45·0
	O_2 -	*nil*	0·45	0·20	0·5
	C_2H_6	42·1	43·60	41·75	45·0
Ratio C/A for the residual gas exploded in the analysis of the products - - - -		1·250	1·247	1·253	1·260
Other observations - - -		(i) No carbon separated. (ii) Steam condensed on cooling, but no hydrogen liberated. (iii) Marked aldehyde-formation. (iv) Percentage contraction would only have been about 31 had the hydrocarbon been burnt to CO_2, CO, and H_2O without aldehyde formation. (v) A high CO_2/CO ratio in circumstances which precluded any oxidation of CO.			

Mixtures containing more than an equimolecular proportion of oxygen were much less reactive than any of the foregoing, although the general course of the oxidation was, in all essential respects, the same, as the following tabulated results shew (Table XCVI). Attention is specially directed to the marked retarding effect of excess oxygen, beyond the equimolecular proportion, upon the oxidation process.

Table XCVI.—Results of Bulb Experiments with $C_2H_6+2O_2$ and $C_2H_6+3{\cdot}5O_2$ Mixtures at 300° C. (Bone and Stockings)

Mixture		$C_2H_6+2O_2$		$C_2H_6+3{\cdot}5O_2$	
Duration of heating		90 mins.	18 hrs.	17 hrs.	48 hrs.
Percentage contraction		35·7	44·5	33·3	37·0
Percentage composition of N_2-free gaseous products	CO_2	14·75	28·45	15·05	20·80
	CO	34·60	59·10	32·50	36·20
	O_2	25·40	0·20	44·40	37·50
	C_2H_6	23·05	10·40	8·05	5·50
	CH_4	2·20	1·85	*nil*	*nil*
Ratio C/A for the residual gas exploded in analysing the products		1·282	1·310	1·25	1·25
Other observations		Neither carbon nor hydrogen liberated, but steam condensed in cooling; rinsings gave an aldehydic reaction.			

Experiments with Ethylene and Acetylene at 300° C.

(*a*) *In* 65 *c.c. Bulbs.* Numerous experiments were also made with ethylene-oxygen and acetylene-oxygen mixtures respectively, in varying proportions, such as 2 : 1, 1 : 1, 1 : 2, etc., at 300° C., with results generally resembling those which had previously been obtained with the corresponding ethane-oxygen mixtures. The equimolecular mixtures were again the most reactive, the whole of the oxygen disappearing within an hour. The 2 : 1 (*i.e.* $2C_2H_4+O_2$ or $2C_2H_2+O_2$) mixtures were, however, almost as reactive; but with excess of oxygen beyond the equimolecular proportion the oxidation process slowed up considerably. Neither carbon nor hydrogen was liberated, but steam was abundantly produced and condensed on cooling. There was always a marked aldehyde formation, and in three separate experiments with an $C_2H_4+2O_2$ mixture *a marked production of formaldehyde was observed without any appreciable production of steam or oxides of carbon,* shewing that in the oxidation of ethylene the aldehyde formation precedes that of the other products mentioned, a most important result from the theoretical standpoint. In the case of acetylene there was some indication of an oxygenated molecule—$C_2H_2O_2$—being the initial oxidation product. The results of a few typical experiments are shewn in the following two tables :

TABLE XCVII.—RESULTS OF BULB EXPERIMENTS WITH ETHYLENE-OXYGEN MIXTURES AT 300° C. (BONE AND WHEELER)

Mixture - - -		$2C_2H_4+O_2$	$C_2H_4+O_2$	$C_2H_4+2O_2$	$C_2H_4+2O_2$
Duration of heating -		30 mins.	30 mins.	30 mins.	20 hrs.
Percentage contraction		27·1	40·0	Very small	40·0
Percentage composition of N_2-free gaseous products -	CO_2 -	4·70	10·0	Formation of aldehyde observed without any appreciable production of CO_2, CO or H_2O	29·5
	CO -	23·75	65·8		66·7
	O_2 -	7·35	*nil*		0·3
	C_2H_4	63·50	17·5		2·5
	C_2H_6	0·70	6·5		1·0
Other observations -		Neither carbon nor hydrogen liberated, but usually steam condensed on cooling; rinsings always gave strong aldehydic reaction.			

TABLE XCVIII.—RESULTS OF BULB EXPERIMENTS WITH ACETYLENE-OXYGEN MIXTURES at 300° C. (BONE AND ANDREW)

Mixture - - -		$2C_2H_2+O_2$	$C_2H_2+O_2$	$C_2H_2+1\frac{1}{2}O_2$	$C_2H_2+3O_2$
Duration of heating -		30 mins.	30 mins.	3 hrs.	3 days
Percentage contraction		24·8	27·9	23·9	21·0
Percentage composition of N_2-free gaseous products -	CO_2	9·5	15·85	22·05	18·60
	CO -	36·9	58·05	56·50	36·35
	C_2H_2	53·3	25·35	10·80	2·15
	C_2H_6	0·2	0·25	0·20	0·30
	H_2 -	0·1	0·50	0·35	nil
	O_2 -	*nil*	*nil*	10·10	42·60
Other observations -		No carbon liberated; steam always formed, and rinsings always gave a strong aldehyde reaction (formaldehyde). In one case indications of the initial formation of $C_2H_2O_2$ were obtained.			

(*b*) *In a* 485 *c.c. Glass-Globe.* A few special experiments were made in which an equimolecular mixture of either ethylene and oxygen or acetylene and oxygen was sealed up at atmospheric temperature and pressure in a borosilicate glass globe of 485 c.c. capacity. The vessel was afterwards maintained at 300° to 350° for three or four hours, by which time the oxidation process was completed. In this way the reaction products from a fairly large volume of the gaseous mixture could be examined. No carbon was deposited, nor was there ever any material liberation of hydrogen; but on cooling large quantities of steam condensed, and the gaseous products were always under a greatly reduced pressure, and had an overpowering aldehydic smell. The condensed liquid also always gave a strong aldehydic reaction; that resulting from the ethylene-oxygen experiment contained both acetaldehyde and formaldehyde, but no ethylene oxide or ethyl alcohol; in the case of the acetylene-oxygen experiment formaldehyde only could be detected. Most likely with the ethylene-oxygen mixture vinyl alcohol had been initially formed, some of which had changed over into the isomeric acetaldehyde, an observation which was confirmed by other experiments. The results of a typical experiment with each of the two mixtures in question are tabulated below:

TABLE XCIX.—RESULTS OF EXPERIMENTS IN A 485 C.C. GLASS GLOBE WITH ETHYLENE-OXYGEN AND ACETYLENE-OXYGEN MIXTURES (BONE, WHEELER AND ANDREW)

Original mixture - - . -	(*a*) $C_2H_4+O_2$	(*b*) $C_2H_2+O_2$
Initial pressure (at 17° to 20°C.)	757	730 mm.
Final pressure of dry products (at 17° to 20° C.) -	455	547 mm.
Percentage composition of N_2-free gaseous products -	$CO_2=15{\cdot}75$ $CO=53{\cdot}75$ $C_2H_4=29{\cdot}10$ $C_2H_6=\ 1{\cdot}40$ $H_2=nil$ $O_2=nil$	$CO_2=20{\cdot}8$ $CO=52{\cdot}75$ $C_2H_2=25{\cdot}15$ $H_2=\ 1{\cdot}05$ $O_2=\ 0{\cdot}25$
Other observations - -	(i) No carbon deposited—but steam condensed. (ii) Products had a pungent aldehydic smell; those from (*a*) containing aldehyde and formaldehyde, but those from (*b*) formaldehyde only.	

Recapitulation of Results of the Bulb Experiments

It will perhaps be convenient now briefly to summarise the most salient features of the evidence derived from the foregoing experiments. This may best be done by concentrating attention upon the new facts established in common for the four hydrocarbons in question, which were as follows:

(1) All four hydrocarbons examined are capable of quiet non-explosive

interaction with oxygen at temperatures between 300° and 350° C., with the production of steam, aldehydes, and both oxides of carbon, in circumstances precluding any appreciable oxidation of either hydrogen or carbonic oxide.

(2) Methane is decidedly less susceptible to oxidation than the other three, between whose oxygen-affinities there seems little to choose.

(3) As regards each of the three hydrocarbons ethane, ethylene and acetylene, whilst an equimolecular mixture with oxygen is the most reactive in the circumstances referred to, and the 2 : 1 (*i.e.* $2C_2H_6 + O_2$, etc.) mixture is not far behind it, any excess of oxygen beyond the equimolecular proportion retards the process.

(4) In *all* cases aldehyde formation is prominent at an early stage in the oxidation; but whilst in the cases of the two saturated hydrocarbons, methane and ethane, such formation undoubtedly occurs simultaneously with that of steam, in the case of ethylene definite evidence was forthcoming that it precedes any formation of either steam or oxides of carbon. In the case of acetylene there was an indication of an oxygenated molecule $C_2H_2O_2$ being transiently formed as the initial oxidation product, and giving rise to CO and formaldehyde before any steam appeared.

(5) Another outstanding feature of the oxidation process in *all* cases was the persistent production of carbon dioxide in circumstances precluding its arising from the secondary oxidation of the monoxide. This fact is of considerable significance, and any valid theory of the process must be capable of explaining it.

The Circulation Method

Apparatus and Operation. In order to be able to follow with pressure records the whole course of the oxidation, and to obtain larger quantities of condensable or soluble intermediate products than was possible under the conditions of the bulb experiments, the ‘circulation apparatus’ was devised. It consisted essentially of a closed system in which the reacting gases (a mixture of some hydrocarbon and oxygen in known proportions) were continuously circulated, at a constant rate, round a closed system containing (*a*) as the ‘reaction zone,’ a combustion tube packed with fragments of porous porcelain and kept at some uniform temperature—usually between 400° and 500° C.—at which the gases would combine at a convenient speed, (*b*) some suitable cooling and condensing arrangement to ensure the rapid removal of condensable or soluble products, and (*c*) a manometer.

The apparatus actually used in the experiments now under consideration is shewn diagrammatically in Fig. 143, and its operation will be perhaps made clearer if we suppose it to have been previously set going with some hydrocarbon-oxygen mixture under investigation, and follow the course of the gases round the circuit. The starting-point is the glass globe *A* (capacity 1200 c.c.) which serves as a reservoir for the circulating gases; in the actual experiments it always contained a few cubic centimetres of distilled water, so that the gaseous mixture was kept saturated with water vapour at a temperature $t°$ indicated by a thermometer placed against the globe with its bulb actually touching the outer wall. The globe was carefully screened by asbestos cardboard both from radiation and from draughts. On leaving the globe the gases traversed the Jena glass combustion tube, *BC* (length 75 cm.), filled with fragments of ignited porous porcelain; each end of the tube was drawn out to the diameter of ordinary quill tubing in such a manner that the narrower portions project several inches beyond the bed of the constant temperature furnace on which the tube rested. The two joints, *a* and *b*, connecting *BC* with the rest of the apparatus were made with very stout indiarubber pressure tubing, the two glass ends underneath being gradually pushed together until they actually came into contact; with these two exceptions all the other joints in the apparatus were fused together by means of the blowpipe.

On leaving the combustion tube the gases passed first through the glass worm, *E*, containing distilled water, and then through the long glass spiral, *F*. Both *E* and *F* were surrounded by a water-jacket through which a stream of cold water was maintained throughout the experiment in order to ensure the rapid cooling of the hot gases. Since the mixture entered the combustion tube saturated with moisture at the ordinary temperature any steam produced by the interaction of the gases, as well as any soluble or condensable intermediate product which survived the passage over the heated surface, would be condensed or absorbed in this part of the apparatus.

The cooled gases passed onwards to the automatic Sprengel pump, *L*, through the triangular arrangement *GHK*. The pump delivered the gases into the vertical manometric tube *M*, standing over mercury in the vessel *N*; thence they passed forward through the horizontal tube *P*, round the curve *Q*, past the T-piece *R*, back into the globe *A*, thus completing the circuit. A millimetre scale placed behind the manometer *M* enabled the pressure of the moist gases to be read at regular intervals, the automatic Sprengel pump being thrown out of action for a moment by shutting the tap *p*.

The apparatus was closed by the glass tap *c*, working in a mercury cup and sealed into the vertical branch of the T-piece *R*. On the other side of *c* was sealed the glass T-tap *d*, through which communication could be made with either (1) the glass gas-holder containing the mixture to be investigated, or (2) an auxiliary Sprengel pump (not shown in the diagram). This latter was used either during the preliminary exhaustion of the apparatus or (if necessary) for the removal of samples of gases during the course

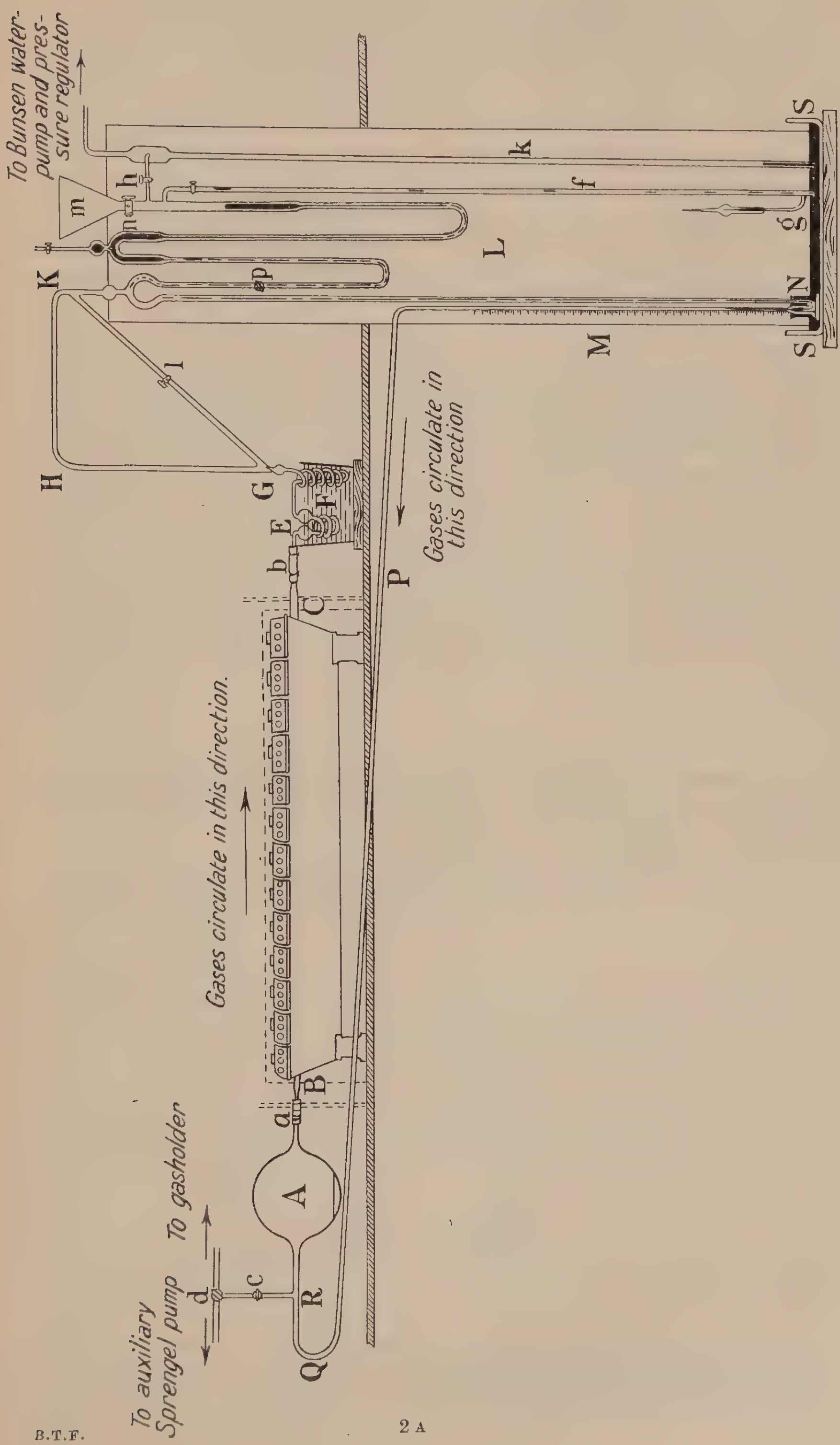
To Bunsen water-pump and pressure regulator
K
m
h
n
p
L
k
f
g
S
N
J
S
M
H
l
G
F
E
b
C
P
Gases circulate in this direction
Gases circulate in this direction.
B
a
A
To gasholder
c
d
R
Q
To auxiliary Sprengel pump

FIG. 143.—CIRCULATION APPARATUS.

of an experiment. All the joints between this auxiliary pump or the gas-holder and the tap *c* were fused by means of the blowpipe.

The total capacity of the apparatus was about 1450 to 1500 c.c., and when filled under 600 mm. pressure it contained 1150 to 1200 c.c. of the mixture under examination (measured under atmospheric pressure). The speed at which the mixtures were circulated, although constant throughout a given experiment, could be varied in different experiments, and was usually such that a circuit would be completed once in one or two hours, each portion of the gases remaining about three to six minutes in the combustion tube during each cycle.

Experimental Results. It will perhaps suffice if the results of one typical experiment are detailed, and the remainder summarised. It should, however, be understood that the conditions were in some respects different from those of the bulb experiments; for the gaseous mixtures were now reacting at a higher temperature (450° to 500° C. instead of at 300 to 350° C.) but at a much lower pressure than in the bulb experiments; also, there was now a catalysing surface in the reaction zone, and any water soluble and condensable products were quickly and continuously removed from the system almost as fast as they were formed. It should be added, also, that (unlike those of the bulb experiments) the conditions now admitted of the independent oxidation of either hydrogen or carbonic oxide.

Typical Experiment with an $C_2H_6+O_2$ *Mixture at* 500° C.

This experiment extended over three days, the temperature of the reaction tube remaining very constant throughout; the gaseous mixture was circulated as rapidly as the pump would work.

Pressure of cold dry-N_2-free original mixture at 17·5° = 467·6 mm.*
" " " final products at 17·5° = 263·5 mm.*
Fall = 204·1 mm.

The pressure fall, which in all amounted to 43·66 per cent. of the original pressure, was continuous throughout the experiment, thus:

Days.	Temperature of Combustion Tube.	Corrected Pressure of Dry N_2-Free Gas. mm.
0	500°	490·7
1	502°	416·0
2	500°	344·3
3	503°	276·2
		Fall = 214·5

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* These pressures relate to the apparatus "all cold"; when the 'combustion tube' was at 500° C. they were 490·7 and 276·2 mm. respectively.

The partial pressures of the original gases and the final gaseous products at 17·5° were as follows :

Original Mixture.	Products.		
mm.	mm.	mm.	mm.
C_2H_6=232·5	CO =42·1	C_2H_6=134·4	H_2= 3·5
O_2=235·1	CO_2=55·2	C_2H_4= 7·2	O_2=21·1
467·6	Total=263·5 mm.		

There was no sign whatever of any deposition of carbon on the white porous porcelain during the experiment, a remark which equally applies to *all* other similar experiments with hydrocarbon-oxygen (or air) mixtures.

It thus appeared that, whereas 90·9 mm. (*i.e.* 232·5 *minus* 134·4 and 7·2 mm.) of ethane had been oxidised during the experiment, the sum of the partial pressures of the oxides of carbon at the end of it was 97·3 mm. only, a circumstance pointing to a large formation of some condensable or soluble intermediate product. And, consistently with such observations, the liquid in the worms *E* and *F* at the end of the experiment was found to contain formaldehyde, which was identified by means of its p. bromophenyl-hydrazone. Indeed, the ‘ balance ’ of the experiment worked out as though :

	mm. O_2
84·1 mm. of ethane had been oxidised through acetaldehyde to $CO + CH_2O + 2H_2O$,* requiring -	168·2
6·6 mm. of ethane had been oxidised to $2CO + 3H_2O$, requiring - - - - - - - - -	16·5
and 55·2 mm. of CO had been independently oxidised to CO_2, requiring - - - - - - - - -	27·6
Total - - -	212·3 mm.

Oxygen actually used=(235·1 less 21·1)
=214·0 mm.

By means of such ‘ circulation experiments,’ of which a great many were carried out, the intermediate formation of considerable quantities of the following aldehydic products was confirmed, as follows :

(i) In the case of a $2CH_4 + O_2$ mixture, a yield of formaldehyde equivalent to 22 per cent. of the methane burnt was obtained.

(ii) In the case of an $C_2H_6 + O_2$ mixture, both acetaldehyde and formaldehyde were obtained : in one case the yield of formaldehyde was actually 93 per cent. of that required on the supposition that the oxidation had taken place in accordance with the scheme:

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* In other similar experiments acetaldehyde as well as formaldehyde was identified in the products, and there was the strongest internal evidence of its intermediary formation ; also definite proof was obtained that, under the experimental conditions it would be rapidly oxidised to $CO + CH_2O + H_2O$.

$$CH_3 \cdot CH_3 + O_2 = (CH_3 \cdot CHO + H_2O) + O_2 = CO + CH_2O + 2H_2O.$$

(iii) In the case of an $C_2H_4 + O_2$ mixture formaldehyde was always obtained, in amounts usually between 30 and 40 per cent. of that required on the supposition that the oxidation had followed the course

$$C_2H_4 + O_2 = (C_2H_4O_2) = 2CH_2O, \text{ etc.}$$

In the case of moist acetylene-oxygen mixtures the evidence was complicated by the circumstance that, as was found, the hydrocarbon readily combined with steam in contact with the hot porcelain surface in the reaction tube, forming acetaldehyde. For this reason the results, which shewed the formation of both acetaldehyde and formaldehyde, could not be considered so conclusive as in other cases in regard to the mechanism of the oxidation process. There was, however, other strong evidence not open to such objection derived from the large globe experiments of both $C_2H_2O_2$ and formaldehyde being intermediate products in the slow combustion of acetylene.

Other Experiments

When it had been proved beyond all possible doubt that such aldehydes are so largely produced during the slow combustion of the hydrocarbons in question, and a good experimental basis had been established for the view that, in the case of ethane, for example, the oxidation involves a primary ‘ hydroxylation ’ of the molecule, in some such manner as,

$$C_2H_6 + O_2 \rightarrow [C_2H_4(OH)_2] \rightarrow CH_3 \cdot CHO + H_2O, \text{ etc.,}$$

the question naturally arose as to whether *ethyl-alcohol* C_2H_5OH or the unstable *dihydroxy-ethane* is the initial product. At first, the fact that in none of the circulation experiments with ethane-oxygen mixtures could any formation of ethyl-alcohol be detected suggested the initial formation of *dihydroxy-ethane.* When, however, it was found that, under such conditions, not only (*a*) does ethyl-alcohol react with oxygen far more rapidly than does ethane, but also (*b*) that its oxidation stages, like those of ethane, involve the successive formations of (i) acetaldehyde, and (ii) formaldehyde, together with considerable quantities of carbonic oxide, etc., and that (*c*) acetaldehyde reacts with oxygen, yielding as the first recognisable product, formaldehyde, carbonic oxide, and steam,

$$CH_3 \cdot CHO + O_2 = CH_2O + CO + H_2O,$$

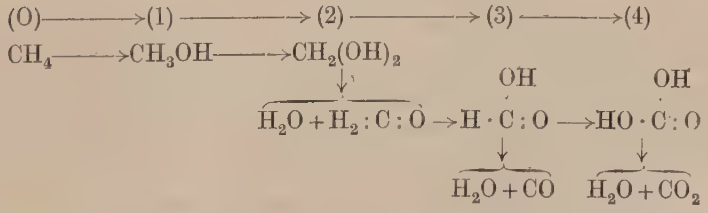
it seems reasonable to suppose that *ethyl-alcohol* is actually produced initially in the slow combustion of ethane, but is so rapidly further oxidised to the unstable *dihydroxy-ethane* that ordinarily it cannot be isolated. Moreover, when ethyl-alcohol, together with acetaldehyde and acetic acid, was found among the products of the interaction of ethane and ozone at both 15° and 100° C.* there could no longer be much doubt as to its really being the initial oxidation product. Such facts, together with observations that *vinyl alcohol* (rapidly changing over to the isomeric *acetaldehyde*) is initially formed during the slow combustion of ethylene, constituted a strong chain of evidence in favour of the view that the slow combustion of a hydrocarbon is essentially a process of ‘ hydroxylation.’

The Hydroxylation Theory of Hydrocarbon Combustion

The idea underlying this theory is that, when a hydrocarbon is oxidised, there is a natural tendency for its hydrogen atoms to be successively converted into OH groups, thus producing ‘ hydroxylated ’ molecules with consequent heat evolution. The stability of such molecules would vary very greatly with temperature and other circumstances ; some of them, more particularly those containing two such OH groups attached to one and the same carbon atom, would be very unstable in any circumstances, and would quickly decompose into stabler products. Thus, for example, the almost instantaneous decomposition of *dihydroxy-methane* into formaldehyde and steam is readily understood. The theory, therefore, supposes that the course of the slow oxidation of such hydrocarbons as methane, ethane and ethylene is essentially one of successive ‘ hydroxylation ’ stages, with evolution of heat, accompanied by (according to circumstances) the thermal decomposition of unstable ‘ hydroxylated ’ molecules into simpler products, which latter may undergo further oxidation in like manner. And, according to such a view, neither steam nor oxides of carbon are *immediate* oxidation products, but arise as the result of thermal decomposition of unstable hydroxylated molecules. In the case of acetylene, however, it seems possible that an oxygenated molecule $C_2H_2O_2$ is the initial product. The theory will, perhaps, be best understood by considering the following schemes shewing how it would explain the slow combustion of methane, ethane and ethylene at temperatures between 300° and 400° C. :

Scheme for Slow Combustion at 300° *to* 400° C.

Stage. (*a*) *Methane*



$$\begin{array}{l}
(0)\longrightarrow(1)\longrightarrow(2)\longrightarrow(3)\longrightarrow(4) \\
CH_4\longrightarrow CH_3OH\longrightarrow CH_2(OH)_2 \\
\qquad\qquad\qquad\qquad\qquad\downarrow \\
\qquad\qquad\quad \overbrace{H_2O+H_2:C:O}\longrightarrow H\cdot\overset{OH}{C}:O\longrightarrow HO\cdot\overset{OH}{C}:O \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\downarrow\qquad\qquad\quad\downarrow \\
\qquad\qquad\qquad\qquad\qquad\qquad \overbrace{H_2O+CO}\quad \overbrace{H_2O+CO_2}
\end{array}$$

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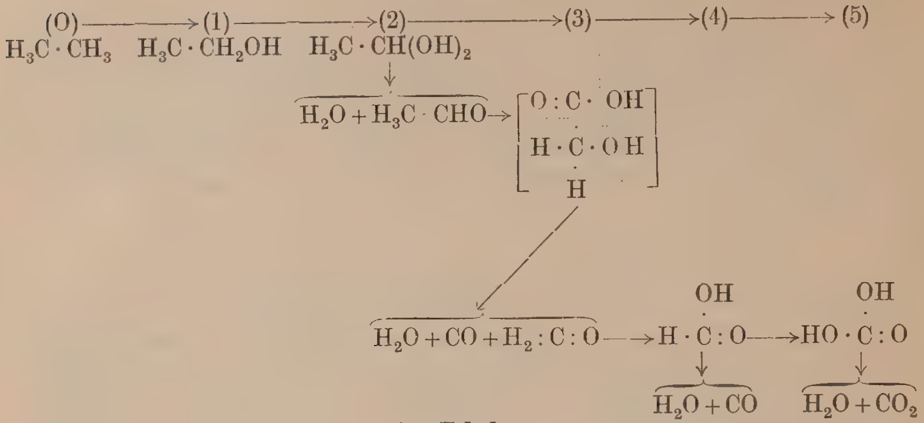
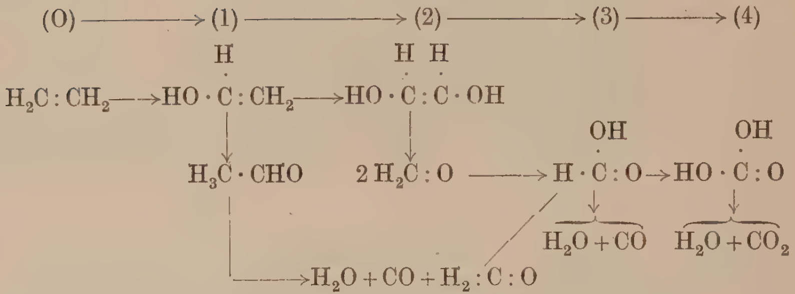
* J. Drugman, *Trans. Chem. Soc.* 89 (1906), pp. 939 to 945.

(*b*) *Ethane*



(*c*) *Ethylene*



It may be added that independent confirmation of the theory was forthcoming from an investigation carried out in 1922–3 by T. S. Wheeler and E. W. Blair at the R.N. Cordite Factory, Holton Heath (Dorset), for the Chemistry Board of the Department of Scientific and Industrial Research on the Oxidation of Hydrocarbons with Special Reference to the Production of Formaldehyde.* These authors, using a modified form of Bone's circulation apparatus, made a detailed study of the slow oxidation of methane and ethylene in it, with results which were in complete agreement with the theory. In the case of ethylene they obtained a large yield of acetaldehyde, arising by intramolecular change from the unstable vinyl alcohol which undoubtedly is the initial oxidation product, as Bone and R. V. Wheeler had found nearly twenty years previously.†

It should not be thought, however, that the subject is exhausted, for as yet some important areas of it have been little explored. No doubt a detailed study of the slow combustion of some of the higher paraffins and olefines would yield interesting results, and next to nothing is known concerning the mode of combustion of aromatic and other cyclic hydrocarbons, which conceivably may be different from that of paraffins and olefines.

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* *Journ. Soc. Chem. Ind.* **41** (1922), p. 303 T., and **42** (1923), 81, 87 and 415 T.

† *Trans. Chem. Soc.* 85 (1904), pp. 1637-1663.

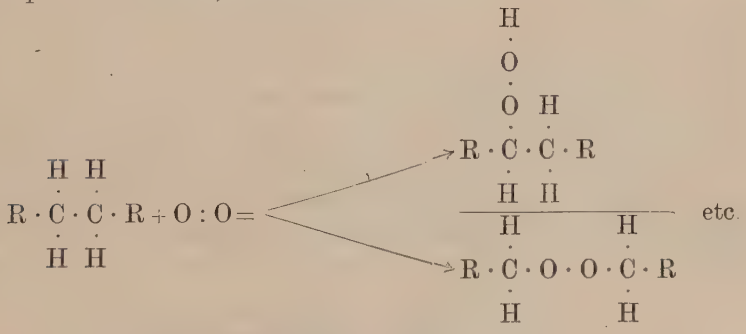
And we ought not to rest satisfied until such wider knowledge has been attained.

Quite recently, however, researches carried out under the direction of H. L. Callendar at the Imperial College, London, upon the combustion of higher paraffins have partly made up our deficiencies in this direction. It has been found, in conformity with Bone's previous observation that the slow combustion of ethane commences at a lower temperature than that of methane, that what Callendar terms the 'temperature of initial combustion' (T.I.C.)—meaning thereby the lowest temperature at which mixtures of the hydrocarbon vapours with air begin to react appreciably—falls as the paraffin series is ascended ; the same applies also in the benzene series. Thus he found, under the conditions of his experiments :

Paraffin Series.	T.I.C.	Benzene Series.	T.I.C.
Pentane	295°	Benzene	670°
Hexane	266°	Toluene	550°
Nonane	210°	Xylene	540°
Undecane	200°		

In regard to the slow combustion of hexane, which he specially studied, Callendar found that "aldehydes, *i.e.* acetaldehyde, formaldehyde, valeraldehyde, etc., are formed in great profusion. It was computed that at 370° C. the aldehydes accounted for 45 per cent. of the hexane consumed, and at 500° C. for as much as 67 per cent., but at still higher temperatures, exceeding 550° C., the aldehyde yield decreases owing to the thermal decomposition of these compounds." *

Also, just as Bone and Stockings never found ethyl-alcohol among the products of the slow interaction of ethane and oxygen (or air), so Callendar could obtain no evidence of any mono-hydroxy-compound (*e.g.* $C_6H_{13} \cdot OH$ or the like) in his experiments on hexane. For this reason he considers that the initial oxidation of a hydrocarbon in air more probably involves the formation of an alkyl peroxide "by the direct incorporation of the oxygen molecule in the hydrocarbon molecule and after direct collision," such peroxide subsequently giving rise to aldehydes and water as decomposition products. Thus, he would write :



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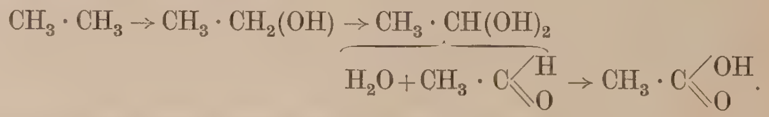
* *Engineering*, 123 (1927), pp. 147-8, 182-4, and 210-2.

To this it may be replied that, whilst the suggested initial peroxide-formation is a possibility, the failure to find an alcohol among the products of the interaction of a hydrocarbon and oxygen is no good reason for doubting its transient production in such circumstances; because, as Bone and Stockings found more than twenty years ago, ethyl-alcohol reacts with oxygen (or air) far more rapidly than does ethane at the same temperature.* Thus, whereas it was found that no ethyl-alcohol in a mixture of air saturated with its vapour at 35° C. ($C_2H_5 \cdot OH = 105$ mm., $O_2 = 136$ mm. and $N_2 = 514$ mm.) survived a single rapid passage over a catalysing surface of porous porcelain, being wholly converted into acetaldehyde and formaldehyde, a similar ethane-air mixture containing,

$$C_2H_6 = 80 \text{ mm.}, \quad O_2 = 90 \text{ mm.}, \quad N_2 = 340 \text{ mm.},$$

had to be continuously circulated over it at the same temperature for upwards of 48 hours (during which at least 50 circuits would be completed) before interaction ceased. Callendar's statement that "hexane at 420° C., with sufficient air, is for the most part oxidised to aldehydes, etc., whereas ethyl-alcohol at this temperature, and constituting only 10 per cent. of the mixture, was only slightly attacked, the aldehyde content of the products of combustion being only 2 per cent. of the alcohol consumed" is hardly relevant in such connection, because no valid comparison can be made except between a given alcohol and its corresponding hydrocarbon, especially in view of the fact that the higher up the series the more easily is a paraffin oxidised.

It may, however, be emphasised what substantial grounds there are for believing that the initial product of the oxidation of a paraffin or olefine is a *mono-hydroxy* body rather than a peroxide. Thus, in the first place, when J. Drugman subjected ethane to the action of ozone at 100° C., in which circumstances it does not appreciably react with ordinary oxygen, ethyl-alcohol as well as acetaldehyde and acetic acid, were all prominently formed, as though the oxidation had proceeded in successive 'hydroxylation' stages,† thus:



$$CH_3 \cdot CH_3 \rightarrow CH_3 \cdot CH_2(OH) \rightarrow \underbrace{CH_3 \cdot CH(OH)_2}$$
$$H_2O + CH_3 \cdot C\begin{matrix}\diagup H \\ \diagdown O\end{matrix} \rightarrow CH_3 \cdot C\begin{matrix}\diagup OH \\ \diagdown O\end{matrix}.$$

Secondly, there is the significant fact that in Bone's 'bulb experiments' (*q.v.*) upon ethane-oxygen, ethylene-oxygen and acetylene-oxygen mixtures, respectively, at 300° C., whereas there was little to choose between the observed rates of reaction with hydrocarbon oxygen ratios 2 : 1 and 1 : 1, respectively, any excess of oxygen beyond the equimolecular proportions always slowed down the rate considerably. Thirdly, the fact that acetaldehyde, doubtless, arising by intramolecular change from the unstable vinyl-alcohol, is prominent among the products of the slow combustion of ethylene accords much better with a 'hydroxylation' than a 'peroxidation' view of the matter. Lastly, certain outstanding features of the explosive combustion of olefines, which will be referred to in our next chapter, seem to require the 'hydroxylation' view. Indeed, there was only one observation made by Bone and his co-workers that could be regarded as pointing the other way, namely, the transient formation of a substance which seemed to be a *polyglycolide* $n(C_2H_2O_2)$ during the slow combustion of acetylene.*

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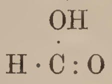
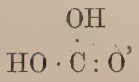
* *Trans. Chem. Soc.* 85 (1904), pp. 719 to 724.

† *Trans. Chem. Soc.* 89 (1906), pp. 939 to 945.

The difference between the two views is, however, chiefly of academic interest and for practical purposes of no great moment, because both agree in regarding the combustion of a hydrocarbon as involving the primary incorporation of the oxygen in the hydrocarbon molecule, with the formation of an 'oxygenated' molecule which subsequently decomposes giving rise to aldehydes, etc., as the principal intermediate products. In other words, according to both views, the immediate result of the initial encounter between hydrocarbon and oxygen is the formation of an 'oxygenated' molecule, which is perhaps the best general view of the matter, although 'hydroxylation' explains most of the known facts much better than 'peroxidation.' The two views are, however, not mutually exclusive, and may perhaps be supplementary; for only a very rash or dogmatic person would nowadays assert that *every* collision between hydrocarbon and oxygen molecules (or oxygen atoms) must always have precisely the same result as regards the particular 'oxygenated' molecule initially produced.

Besides providing a view-point of such slow combustions which appeals to the organic chemist and obviates all the difficulties inherent in the former ideas of 'preferential combustion,' the hydroxylation theory readily explains one outstanding fact, to which attention has been repeatedly directed in this chapter, namely, the persistent formation of so much carbon dioxide during the bulb experiments with methane, ethane, ethylene and acetylene in circumstances which absolutely precluded its arising by the oxidation of carbonic oxide. For, it is now seen to arise as the result of the oxidation of *formic acid*  $H\cdot\overset{OH}{\dot{C}}:O$ to *carbonic acid*  $HO\cdot\overset{OH}{\dot{C}}:O$, which, being unstable, instantly breaks down into anhydride and steam. In this connection also the 'hydroxylation' view is much preferable to any other yet advanced.

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* *Trans. Chem. Soc.* 87 (1905), p. 1235.

CHAPTER XXX

THE EXPLOSIVE COMBUSTION OF HYDROCARBONS

Introduction

Whilst the ‘hydroxylation’ theory was being established for the slow non-explosive combustion of certain typical hydrocarbons at temperatures below ignition, the question naturally arose whether the facts of their explosive combustion could be explained on similar lines. Accordingly, Bone and his collaborators undertook a systematic experimental enquiry into the matter.

At that time some whose opinion on such matters was entitled to carry weight found difficulty in believing that such unstable substances as aldehydes could have even a transient existence at the high temperatures of flames and explosions, and preferred to think of the explosive combustion of (say) ethylene or acetylene as involving, in the first instance, something indistinguishable from a preferential burning of carbon.

Thus, for example, it was said that “The isolation of an intermediate product under one set of circumstances is in itself no proof that this product is transitorily formed when the reaction is proceeding under another set of circumstances.” * We doubt, however, whether nowadays such a point would be urged very strongly. For it could be replied that, whilst doubtless the isolation of (say) acetaldehyde during the slow oxidation of ethane is not *by itself* sufficient proof of its transitory formation in the explosive combustion of the hydrocarbon, yet if it can be demonstrated (1), not only that the ascertained facts of its explosive combustion can be *best* interpreted on such basis, but (2) that no equally satisfactory interpretation can be advanced, and, moreover (3), that aldehydes are actually produced in flames, the difficulty becomes shadowy, even if it did not entirely vanish. In Science a theory should be judged by its ability to give a consistent interpretation of the facts to which it applies, and it may be accepted as a serviceable implement so long as it succeeds in doing so, and until a better one is available. After all, theories are merely tools and vantage points, useful only so long as they best serve as such, and not as objects of veneration, however they may please us.—"Lo, they all shall wax old as a garment; the moth shall eat them up."—So whilst recognising possible limitations to any theory, and the need of revision from time to time as knowledge increases and new facts emerge, we may proceed to examine this one in the light of what is now known.

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* A. Smithell’s Presidential Address to Section B. of the British Association at Leicester, 1907.

It is not difficult to demonstrate the existence of aldehydes in ordinary hydrocarbon flames. Bone and Drugman found them in the interconal gases where ethylene was burnt in air in a modified form of Smithells' separator, as also in the condensed water formed when a steady flame of air (or oxygen) was maintained in an atmosphere of hydrocarbon or coal gas,* in the water-jacketted glass apparatus shewn in Fig. 144. Their presence has also been proved (as will be seen later) in the products when hydrocarbons such as ethane and ethylene are exploded with suitable defect of oxygen. And the sometimes pungent odours of the exhaust gases from petrol-engines is reminiscent of them.

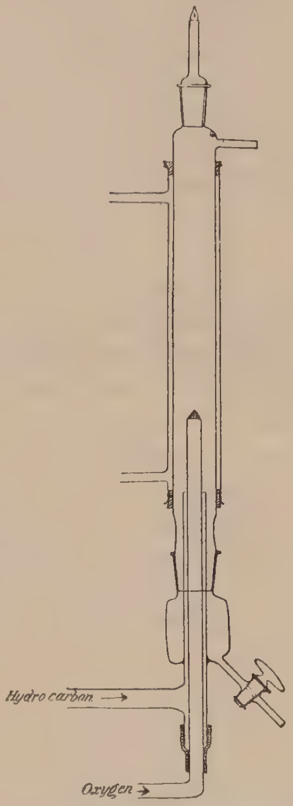

FIG. 144.—WATER-JACKETTED FLAME SEPARATOR. (Bone and Drugman.)

Moreover, as will be shewn later, the only serious alternative theory which has found any wide acceptance during the past thirty-five years—namely that of the preferential burning of carbon—rested upon a few well-known facts, such as the production of carbonic oxide and hydrogen when equimolecular mixtures of ethylene and oxygen, or of acetylene and oxygen, are exploded, thus:

$$(a)\quad C_2H_4 + O_2 = 2CO + 2H_2,$$

$$(b)\quad C_2H_2 + O_2 = 2CO + H_2,$$

which can equally well be explained by the supposition of the *primary* formation of an 'hydroxylated' or 'oxygenated' molecule. It is contradicted, however, by many other equally well established facts, as, for example, the behaviours on explosion of (*c*) an equimolecular mixture of ethane and oxygen, or (*d*) a 60/40 ethylene-oxygen mixture, both of which are quite consistent with, and could have been predicted by, the 'hydroxylation' theory.

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* *Trans. Chem. Soc.* **89** (1906), p. 660.

Another view which has been suggested, namely, that in combustion a hydrocarbon is first of all resolved into its elements, which then react with the oxygen, so that the burning is essentially a distribution of the latter between carbon and hydrogen, the hydrocarbon not coming in at all as such, will hardly bear close examination, and, as will be shewn later, it is contradicted by another group of facts. Moreover, except *possibly* in cases of such highly endothermic ones as acetylene, which decompose explosively at high temperatures or under shock, the rate at which hydrocarbons combine with oxygen so far exceeds that at which they decompose in flames that the idea seems quite untenable.

When we say that the ‘ hydroxylation ’ theory is capable of explaining the explosive combustion of hydrocarbons, we do not mean, of course, that the phenomena observed in slow combustion, at comparatively low temperatures, are exactly reproduced in flames, but rather that the result of the initial encounter between suitably disposed hydrocarbon and oxygen molecules is probably much the same in both cases, namely, the formation of a ‘ hydroxylated ’ or ‘ oxygenated ’ molecule. At the higher temperatures of flames secondary thermal decompositions undoubtedly come into operation at an earlier stage, and play a more important *rôle* than in slow combustion ; they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence of it.

Another consideration which should not be lost sight of is that in flames we are dealing with ‘ ionised ’ molecules, and possibly also charged O atoms ; thus, when (say) ethylene burns, it may be that the ‘ hydrocarbon molecule ’ concerned is not $\begin{array}{c}\mathrm{HCH}\\ \because\\ \mathrm{HCH}\end{array}$, but $\begin{array}{c}\cdot\\ \mathrm{H}\cdot\mathrm{C}\cdot\mathrm{H}\\ \cdot\\ \mathrm{H}\cdot\mathrm{C}\cdot\mathrm{H}\\ \cdot\end{array}$, or even $\mathrm{H}\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot\mathrm{H}$.

Also, we must remember that even nitrogen possibly may not be so inert in flames as was formerly supposed. Anyway, it is well always to keep such possibilities in mind, even if only to prevent our laying too much stress upon particular ‘ equations,’ as though any of them can adequately represent the actualities of flame.

Supposing, then, that in hydrocarbon flames the result of the initial encounter between the oxygen and combustible is the formation of an unstable ‘ hydroxylated ’ or ‘ oxygenated ’ molecule, which soon decomposes unless it be immediately further oxidised, it would be important to know how such substances as alcohols and aldehydes would be likely to decompose in flames. Fortunately, there is a good deal of information about such matters available, which will now be considered.

The Thermal Decompositions of Alcohols and Aldehydes

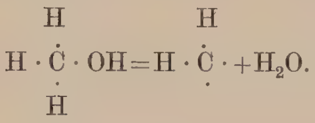
Methyl and Ethyl Alcohols. Ipatiew, in his well-known researches upon the decomposition of alcohols in contact with hot solids,* found that on passing the vapour of ethyl alcohol through a combustion tube heated to between 800° and 830° C., it underwent a twofold decomposition, one-fifth being resolved into ethylene and steam and the remaining four-fifths into acetaldehyde and hydrogen. In a similar experiment with methyl alcohol at 880° C. a very slow decomposition occurred, resulting in the formation of ‘ oxymethylene ’ (CH_2O) and a gas containing

$$CO=16{\cdot}1,\ H_2=76{\cdot}8,\ \text{and}\ CH_4=5{\cdot}4\ \text{per cent.},$$

no carbon being deposited.

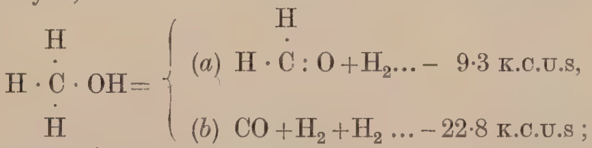
In 1908 W. A. Bone and H. Davies † carried out experiments on the thermal decomposition of methyl alcohol at temperatures between 650° and 1000° C., which led them to view the process as involving simultaneously,

(i) an essentially low-temperature decomposition into $H_2 : C :$ and H_2O, thus ;



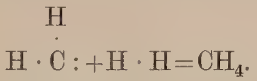
$$H\cdot\overset{H}{\underset{H}{C}}\cdot OH=H\cdot\overset{H}{\underset{\cdot}{C}}\cdot+H_2O.$$

(ii) a high temperature decomposition into, ultimately, $CO+2H_2$ *via* formaldehyde, thus :



$$H\cdot\overset{H}{\underset{H}{C}}\cdot OH=\begin{cases}(a)\ H\cdot\overset{H}{C}:O+H_2\ldots-\ 9{\cdot}3\ \text{K.C.U.S}, \\ (b)\ CO+H_2+H_2\ \ldots-22{\cdot}8\ \text{K.C.U.S};\end{cases}$$

and (iii) the ‘ hydrogenation ’ of the $:CH_2$ residues transiently formed in (i) by the hydrogen liberated during (ii) forming methane



$$H\cdot\overset{H}{C}:+H\cdot H=CH_4.$$

It should be noted that at no temperature between the limits referred to was either any carbon deposited or any acetylene or ethylene formed.

At 650° the final gaseous products contained

$$CO=33{\cdot}0,\ H_2=55{\cdot}75\ \text{and}\ CH_4=11{\cdot}25\ \text{per cent.},$$

shewing that about one-fourth of the alcohol vapours had decomposed according to (i), and the remainder according to (ii), with simultaneous complete hydrogenation of $:CH_2$ residues, thus :

$$\left.\begin{array}{lll} CH_3OH= & H_2C: & +H_2O \\ 3CH_3OH= & H_2 & +5H_2+3CO \end{array}\right\}=\begin{array}{c}\text{Final Gaseous Products.}\\ 3CO+5H_2+CH_4 \\ 33{\cdot}35\quad 55{\cdot}55\quad 11{\cdot}1\ \text{per cent.}\end{array}$$

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* *Ber.* **34** (1901), 3579, **35** (1902), 1047.

† *Trans. Chem. Soc.* **105** (1914), pp. 1691 to 1696.

Such a 'resultant reaction' would still be endothermic, involving on the average $-7{\cdot}5$ K.C.U.s per gram-molecule of the alcohol vapour decomposed. On the other hand, the *resultant* effect of (i) and (ii) occurring equally, with subsequent hydrogenation of the $:CH_2$ residues (*i.e.* $2CH_3OH \rightleftharpoons CO + H_2 + H_2O + CH_4$) would be exothermic, involving in the average $+7{\cdot}8$ K.C.U.s per gram molecules of alcohol decomposed.

With rising temperature decomposition according to (ii) more and more prevailed over (i), until at 1000° the rate of (ii) to (i) was about 17 : 1, with subsequent complete hydrogenation of $H_2C:$ residues to CH_4, the gaseous products containing :

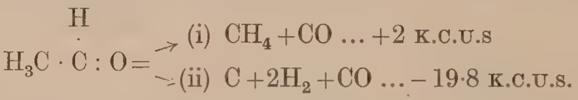
$$CO = 33{\cdot}1,\ H_2 = 64{\cdot}9 \text{ and } CH_4 = 2{\cdot}0 \text{ per cent.}$$

Formaldehyde. W. A. Bone and H. L. Smith found that at all temperatures between 400° and 1125° C., in the absence of a catalysing surface, the formaldehyde vapour decomposes simply into carbonic oxide and hydrogen :

$$H_2:C:O = CO + H_2 \ldots -13{\cdot}5 \text{ K.C.U.s},$$

without any carbon deposition or steam formation whatsoever.

Acetaldehyde. In similar circumstances, the vapour of this substance was found * to decompose (*a*) at 400° C. simply into methane and carbonic oxide, (*b*) and at 600° and above into methane, carbonic oxide, carbon and hydrogen, as represented by the scheme :



$$H_3C \cdot \overset{H}{\dot{C}} : O = \begin{array}{l} \nearrow \text{(i) } CH_4 + CO \ldots +2 \text{ K.C.U.s} \\ \searrow \text{(ii) } C + 2H_2 + CO \ldots -19{\cdot}8 \text{ K.C.U.s.} \end{array}$$

In other words, at *low* temperatures (i) occurs exclusively, but as the temperature rises (ii) comes more and more into play, but never to the exclusion of (i). Therefore, whenever acetaldehyde is formed and decomposed in flames we may expect to find carbon, hydrogen, methane and carbonic oxide all among the products, but more of the two first named and less methane as the flame temperatures rises.

Evidence Derived from the Behaviour of Hydrocarbons when Exploded with Defect of Oxygen

We are now in a position to consider evidence derived from the behaviour of a few representative hydrocarbons—such as methane, ethane, ethylene and acetylene—when exploded under different conditions with defect of oxygen. Three different experimental conditions may be considered as possibly affecting the course of events, namely, (i) the 'inflammation' of such mixtures in closed vessels, which would resemble the condition of ordinary flames, (ii) their 'detonation' in (say) a long leaden coil, where the conditions of combustion would be those of 'adiabatic compression ' as in the explosion wave, and (iii) their combustion under conditions of high initial pressure in steel bombs, when the effects of high ' density ' can be observed without setting up detonation.

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* *Trans. Chem. Soc.* 87 (1905), pp. 910 to 916.

All these conditions have been systematically explored by W. A. Bone and his collaborators, not only for the simple hydrocarbons referred to it but also for some of the higher paraffins (propane and butane) and olefines (propylene and butylene), so that a great deal of information concerning their behaviour is available. Considerations of space, however, compel us to restrict the discussion mainly to what is known concerning the simpler hydrocarbons methane, ethane, ethylene and acetylene, which may be considered as representative of their respective classes.

Experimental Methods

(1) *Inflammation Experiments.* In studying the conditions of ordinary ' inflammation ' Bone and Drugman * chiefly employed the simple method

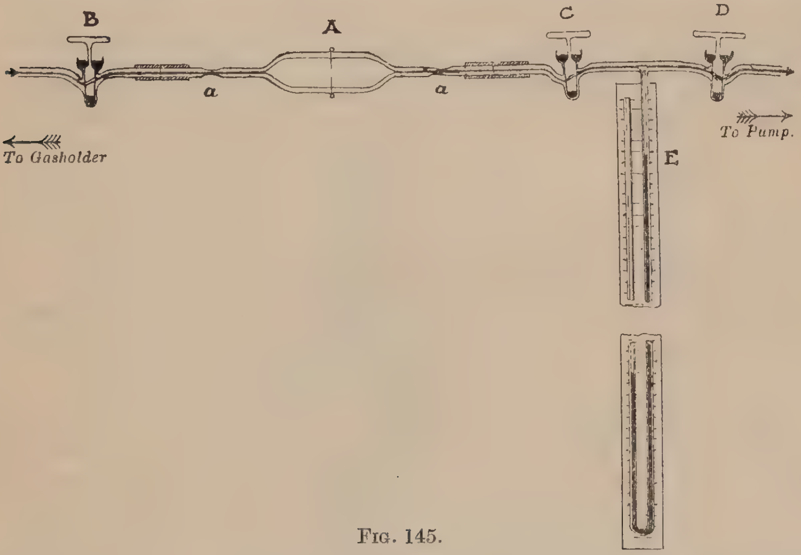

FIG. 145.

shewn in Fig. 145. The explosion vessel was a cylindrical bulb *A* (capacity = 80 c.c.), made of stout borosilicate glass and fitted with platinum firing wires so disposed that the spark ignited the central portion of the explosive medium. Each end of the bulb terminated in a glass tube of narrow bore, somewhat constricted at *a* to facilitate the operation of sealing up the experimental mixture before it was fired. By means of these ends connections were made, as required, either with a glass gas-holder containing the experimental explosive mixture over mercury, or with the capillary manometer, *E*, or with a Töpler pump. For details of the procedure involved in sealing up the experimental mixture at a definite initial pressure (p_1), firing it, and subsequently determining the final pressure (p_2) of the cold gaseous products and their composition, the original papers must be consulted.

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* *Trans. Chem. Soc.* 89 (1906), pp. 660-682 and 1614-1625.

(2) *Comparative Experiments with Long Tube and Large Globe.* In cases when it was desired more particularly to ascertain the influence of different rates of cooling of the explosion flame upon the relative proportion of the various products in the final cold system, comparative experiments were made with the same explosive mixture in two explosion vessels (Figs. 146 and 147) of similar capacity (about 300 c.c.), but with widely different surface area/volume ratio. One of these vessels (A)—*the long tube*—was a glass tube 1 metre long and 2 cms. internal diameter, the mixtures being fired by a spark near one end; the other (B)—*the large globe*—was a globe of 8·5 cms. internal diameter, in which the explosive mixture was fired by a spark at the centre. The surface area/volume ratio of (A) being about three times that of (B), the cooling of the flame in it would be much more rapid than in the other; consequently there would be a greater accumulation of the primary combustion products in A than in B. In this way it is possible to discriminate roughly between the primary (or earlier) and the secondary (or later) products in such explosions, a most important matter from a theoretical point of view.

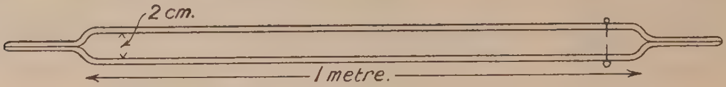

FIG. 146.

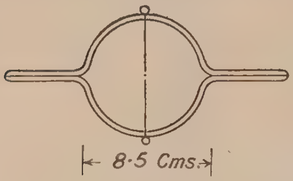

FIG. 147.

(3) *Detonation Experiments.* When the 'detonation' of a hydrocarbon oxygen mixture had to be studied a leaden coil A (Fig. 148) usually about 20 ft. long and 1 inch internal diameter and of a capacity 3100 c.c. was employed. It was set in position in a large water bath, so that its contents could (if necessary) be heated to the boiling point of water just before firing them; or, after an explosion, they could be rapidly cooled by water from the mains. The other end of the coil terminated in a large steel tap C of wide bore, provided with a small side-tap D on the side remote from the coil. The tap C communicated with the firing piece E, composed of stout lead tubing 1 metre long and 12 mm. internal diameter, provided with suitable firing wire fused in through a stout glass-piece F. The other end of this firing piece was closed by a gun-metal cock G. The capacity of the firing piece was 120 c.c.; when desired it could be filled with electrolytic gas after the main part of the coil had been filled with the explosive mixture under investigation, because in some cases it was found necessary to start the

'detonation' in electrolytic gas to ensure its propagation through the mixture.

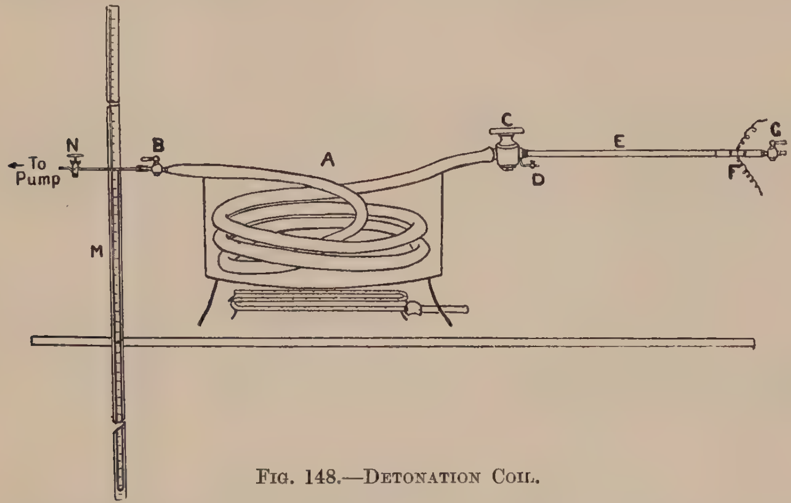

Fig. 148.—Detonation Coil.

(4) *High Pressure Bomb Experiments.* In carrying out explosions under high initial pressures one or other of two explosion bombs was employed, namely, either (*A*) a steel bomb (Fig. 149) with a cylindrical explosion chamber about 8 inches long × 1 inch internal diameter (capacity *circa*

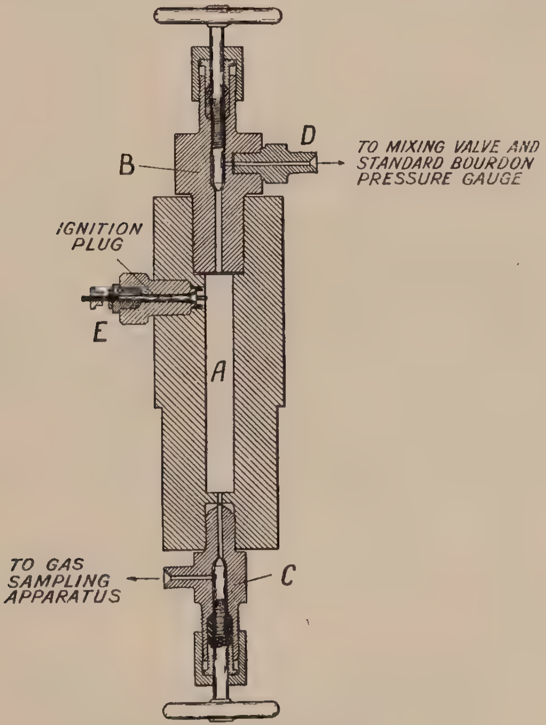
D
TO MIXING VALVE AND STANDARD BOURDON PRESSURE GAUGE
B
IGNITION PLUG
E
A
TO GAS SAMPLING APPARATUS
C

Fig. 149.—Explosion Bomb (*A*).

100 c.c.), or (*B*) the steel bomb with a spherical explosion chamber (capacity *circa* 240 c.c.), with suitable admission valve and firing piece as shewn in Chapter XXII, Fig. 120 (*q.v.*).

Experiments on Methane

As already shewn in Chapter III, it was Dalton who first studied the partial combustion of methane by exploding its equimolecular mixture with oxygen ($CH_4 + O_2$) and finding that the gases combine "without any material change in volume," yielding gaseous products which, after removal of a small amount of carbonic acid, "possess all the characteristics of a mixture of equal volumes of carbonic oxide and hydrogen."

The behaviour of such a mixture on explosion may be illustrated by the following results of two experiments in which it was fired (*a*) in the explosion bulb *A* (Fig. 146) at an initial pressure of 651·6 mm., or (*b*) in a cylindrical bomb (*A*) at an initial pressure of 12·61 atmospheres. In neither case was there any carbon deposition.

TABLE CIV.—RESULTS OF EXPLOSION OF AN EQUIMOLECULAR METHANE-OXYGEN MIXTURE

	Initial and Final Pressures.		p_2/p_1.*	Percentage Composition of the Gaseous Products.				Percentage of Original Oxygen appearing as H_2O in cold Products.
	p_1*	p_2*		CO_2	CO	H_2	CH_4	
(*a*)	651·6 mm.	672·2 mm.	1·031	6·8	41·3	50·8	1·1	43·5
(*b*)	12·61 atms.	14·10 atms.	1.12	7·45	38·5	54·05	*nil*	38·2

In the case of (*b*) the explosion was quite violent, being accompanied by a sharp metallic click. It is clear that in each case the resulting chemical changes had been in accordance with the equations :

$$\left.\begin{array}{ll}\text{In the explosion, -} & \text{(i) } CH_4+O_2=CO+H_2+H_2O\\ \text{During cooling, -} & \text{(ii) } CO+OH_2\rightleftharpoons CO_2+H_2\end{array}\right\}\frac{CO\times OH_2}{CO_2\times H_2}=\overset{(a)}{5\cdot2}\quad\overset{(b)}{3\cdot4}$$

Also, as might be expected in (*a*), the 'water-gas equilibrium' had been 'frozen out' at a higher temperature than in (*b*), where the density of the medium was nearly fifteen times greater.

Such a result is just what might be anticipated from the 'hydroxylation' theory, as the following scheme indicates :

$$\begin{tikzcd} CH_4 \arrow[r, "+O", "+30\ \text{K.C.U.S}"'] & \overset{(1)}{H_3 : C \cdot OH} \arrow[r, "+O", "+59\ \text{K.C.U.S}"'] & \overset{(2)}{H_2 : C : (OH)_2} \arrow[d, "-13\cdot4\ \text{K.C.U.S}"] \\ & & H_2 + CO + H_2O. \end{tikzcd}$$

For, with sufficient oxygen present to carry the system right through to stage (2), a 'non-stop' run through (1) would be most probable ; and, when (2) is reached, 89 K.C.U.s per gram-molecule have been developed, of which only 13·4 need to be absorbed to accomplish the decomposition of the *dihydroxy-methane*, so that the *resultant* heat change would be 75·6 per gram-molecule of methane burnt, or rather less than one-third of its *total* heat of combustion (212 K.C.U.s per gram molecule).

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* In recording these, and all other, experiments in this chapter p_1=the initial pressure of the mixture exploded, and p_2=the pressure of the cooled products, both at room temperature (usually 15 to 18° C.).

Methane-oxygen mixtures containing less than about 60 per cent. of oxygen not being explosive at atmospheric pressure, their combustion had to be studied under high pressure conditions in order to ascertain the effect of progressively reducing the oxygen supply below such proportion. This was done by W. A. Bone and H. Davies, who exploded a series of mixtures of compositions varying between $2CH_4+O_2$ and CH_4+O_2 in the cylindrical bomb *A* already referred to at an initial pressure of about 12·7 atmospheres in each case. The details of these experiments are shewn in Table CV.*

In such circumstances the explosion of a $2CH_4+O_2$ mixture was quite gentle, being almost inaudible, about one-fifth of the carbon present being deposited, and as much as 43 per cent. of the original oxygen appearing as water in the cooled products. Such a result is manifestly quite incompatible with any idea of a preferential combustion of carbon. With an increasing proportion of oxygen in the original mixture the explosion became more audible, until, with the CH_4+O_2 mixture, it was very violent. With a $60CH_4/40O_2$ mixture, however, *no carbon at all was deposited*, and only 28·4 per cent. of the original oxygen appeared as water in the cooled products. On further increasing the proportion of oxygen in the original mixture the proportion of it appearing as water in the cooled products increased, until, with the equimolecular (CH_4+O_2) mixture, it amounted to 38·2 per cent.

Such facts, whilst clearly incompatible with any 'preferential combustion of carbon' idea, are quite consistent with the 'hydroxylation' theory. For the more the oxygen in the original mixture is reduced below the equimolecular the slower will be the combustion, the lower the general temperature, and the greater the tendency for thermal decomposition to occur at the CH_3OH stage. Moreover, in regard to such decomposition, the lower the general flame temperature the more would the 'low temperature' $CH_3OH=H_2C:+H_2O$ decomposition occur, and $:CH_2$ residues therefrom break down into carbon and hydrogen. Indeed the results of the $2CH_4+O_2$ experiment were as though thermal decomposition had taken place at the CH_3OH stage, somewhat as follows:

$$\left.\begin{array}{l} \mathrm{CH_3OH=H_2:C+H_2O=C+H_2+H_2O} \\ \left.\begin{array}{l} \mathrm{CH_3OH=H_2:C\ \ +H_2O} \\ \mathrm{CH_3OH=H_2\qquad +CO+H_2} \\ \mathrm{CH_3OH=H_2\qquad +CO+H_2} \end{array}\right\} \mathrm{=}\begin{array}{l} \mathrm{CH_4+2CO} \\ \quad\mathrm{+3H_2+H_2O} \end{array} \end{array}\right\} \begin{array}{l} \mathrm{C+CH_4+4H_2} \\ \quad\mathrm{+2CO+2H_2O,} \end{array}$$

followed by some $CO+OH_2 \rightleftharpoons CO_2+H_2$, and $C+OH_2 \rightleftharpoons CO+H_2$.

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* The results of a further experimental study of the influence of increasing initial pressures between 6 and 175 atmospheres upon such explosions will shortly be published.

TABLE CV.—EXPLOSION OF MIXTURES OF VARYING COMPOSITION BETWEEN $2CH_4+O_2$ AND CH_4+O_2 IN BOMB *A* AT INITIAL PRESSURE 12·7 ATMOSPHERES. (Bone and Davies.)

Experiment No.	10			11			12			13		
Pressures in atmospheres p_1	12·74			12·72			12·68			12·61		
Pressures in atmospheres p_2	15·05			18·10			17·30			14·10		
p_2/p_1	1·18			1·42			1·36			1·12		
	Per cent.		Partial pressures, atmospheres.	Per cent.		Partial pressures, atmospheres.	Per cent.		Partial pressures, atmospheres.	Per cent.		Partial pressures, atmospheres.
Original mixture CH_4	67·15		8·55	59·3		7·54	55·75		7·09	50·8		6·40
Original mixture O_2	32·85		4·19	40·7		5·18	44·25		5·59	49·2		6·21
	Per cent.		Partial pressures, atmospheres.	Per cent.		Partial pressures, atmospheres.	Per cent.		Partial pressures, atmospheres.	Per cent.		Partial pressures, atmospheres.
Gaseous products CO_2	3·10		0·47	2·70		0·49	3·85		0·67	7·45		1·05
Gaseous products CO	25·40		3·83	35·60		6·44	37·25		6·44	38·50		5·44
Gaseous products CH_4	16·60		2·50	4·65		0·84	2·25		0·39	*nil*		*nil*
Gaseous products H_2	54·90		8·26	57·05		10·32	56·65		9·80	54·05		7·60
	C.	H.	O.	C.	H.	O.	C.	H.	O.	C.	H.	O.
Units in original mixture	8·55	17·10	4·19	7·54	15·08	5·18	7·09	14·18	5·59	6·40	12·80	6·21
Units in gaseous products	6·80	13·26	2·38	7·77	12·00	3·71	7·50	10·58	3·89	6·49	7·60	3·77
Difference atmospheres	1·70	3·84	1·81	—	3·08	1·47	—	3·60	1·70	—	5·20	2·44
Difference per cent.	20		43·2			28·4			30·4			38·2
Ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ in products	3·65			3·75			3·43			3·4		
Remarks	Explosions almost inaudible; carbon deposited.			Explosion distinctly audible. No carbon deposited.						Very violent explosion with sharp metallic click. No carbon deposited.		

Experiments on Ethane

The case of ethane is crucial as between the theories of the preferential combustion of carbon and that of 'hydroxylation'; because, whereas according to the former the equimolecular $C_2H_6+O_2$ mixture should on explosion yield carbonic oxide and hydrogen only, with a p_2/p_1 ratio of 2·5, thus:

$$C_2H_6+O_2=2CO+3H_2,$$

according to the latter it should yield the decomposition products of dihydroxy-ethane and acetaldehyde, as follows:

$$\begin{aligned} C_2H_6+O_2=CH_3\cdot CH(OH)_2&=CH_3\cdot CHO+H_2O \\ &\quad\overbrace{CH_4+CO} \\ &\quad\overbrace{C+2H_2}+CO. \end{aligned}$$

(1) *Inflammation in Sealed Glass Bulb.* On igniting such equimolecular mixture by an electric spark at nearly atmospheric pressure in a sealed borosilicate glass bulb (Method 1, p. 383) of 80 c.c. capacity a lurid flame filled the vessel, accompanied by a black cloud of carbon particles, and when the products cooled abundance of steam condensed. The observed p_2/p_1 ratio was only 1·54; when the vessel was subsequently rinsed out with a little distilled water, and the rinsings filtered from carbon particles, they gave a distinct aldehydic reaction. The results of this important experiment are summarised in Table CVI, as follows:

TABLE CVI.—RESULTS OF EXPERIMENTS ON INFLAMMATION OF AN $C_2H_6+O_2$ MIXTURE IN A SEALED GLASS BULB

Original Mixture.		$C_2H_6+O_2$.		
	p_1	746 mm.		
	p_2	1148 ,,		
	p_2/p_1	1·54		
Percentage Composition of Gaseous Products	CO_2	4·20		
	CO	33·55		
	$C_2H_2+C_2H_4$	2·75		
	CH_4	10·85		
	H_2	48·65		
		C.	H.	O.
Units in original mixture		746	1119	376
Units in gaseous products		621	854	241
Difference		125	265	135
Per cent. Difference		16·8	23·6	36·0

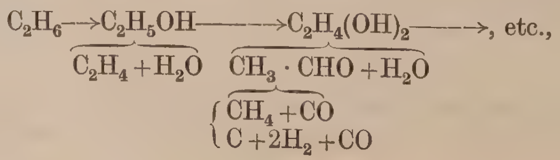
It is thus seen that, besides there having been a considerable carbon deposition and methane formation, no less than 36 per cent. of the oxygen appeared as water in the cooled products. Doubtless the 4·2 per cent. of carbon dioxide found in the gaseous products had arisen from the interaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ during cooling, and simultaneously also some of the steam formed in the explosion would be unburnt by carbon. The results were thus in accordance with the 'hydroxylation' theory, but quite incompatible with that of the preferential combustion of carbon.

(2) *Inflammation in* (*a*) *Large Tube and* (*b*) *Large Globe respectively.* Comparative experiments were next made in which the equimolecular $C_2H_6 + O_2$ mixture was fired in (*a*) the long tube, and (*b*) the large globe (Method 2) referred to on p. 384 (*q.v.*). For, inasmuch as the surface/volume ratio of the former was nearly three times that of the latter, the combustion products would cool down more quickly in (*a*) than in (*b*), a circumstance which would be reflected in a greater survival of the more primary products in (*a*) than in (*b*). In this way it was possible to discriminate in some measure between the earlier and later products.

When the mixture (which actually contained $C_2H_6 = 49{\cdot}5$ and $O_2 = 50{\cdot}5$ per cent.) was ignited near one end of the long tube, at an initial pressure of 701 mm. a bright flame slowly traversed its whole length, at a rate which was judged by the eye to be about half a metre per second, and from a photographic record it appeared that each successive layer of the medium remained incandescent for something between 0·03 and 0·05 second. Some carbon separated in the flame, and much water condensed on cooling. The ratio p_2/p_1 was 1·45, and on subsequently rinsing out the cylinder, and applying Schiff's test to the rinsing, a very strong aldehydic reaction was obtained. The gaseous products contained as much as 5·0 per cent. of acetylene and 2·65 of ethylene.

On repeating the experiment in the large globe (*b*), at an initial pressure of 651 mm. a lurid flame instantly filled the vessel. There was a much greater separation of carbon, but less water condensed on cooling, than in the previous experiment. The p_2/p_1 ratio was now as high as 1·73; the products contained only 0·15 per cent. of acetylene and ethylene, and gave a much fainter aldehydic reaction than previously, though it was still quite distinct.

The results of two such comparative experiments are shewn in Table CVII, from which it would appear that water, unsaturated hydrocarbons, and an aldehyde were primarily produced during the earlier stages of the combustion, carbon being a later product. This is also in accordance with the 'hydroxylation' theory, because if the successive stages in the combustion of ethane are correctly represented as



$$C_2H_6 \longrightarrow \underbrace{C_2H_5OH}_{C_2H_4 + H_2O} \longrightarrow \underbrace{C_2H_4(OH)_2}_{\underbrace{CH_3 \cdot CHO}_{\left\{\begin{array}{l} CH_4 + CO \\ C + 2H_2 + CO \end{array}\right.} + H_2O} \longrightarrow, \text{ etc.,}$$

obviously ethylene would arise at an early stage, as also acetylene, one of its decomposition products. Both steam and acetaldehyde would be formed in large quantities by the decomposition of *dihydroxyethane*, but carbon would be a later product of the breaking down of acetaldehyde and the unsaturated hydrocarbons. Some of the incandescent carbon would subsequently react with steam, so that the longer the duration of the flame or cooling period the less would be the chance of steam surviving.

TABLE CVII.—INFLAMMATION OF AN EQUIMOLECULAR MIXTURE OF ETHANE AND OXYGEN

		A. In Long Tube.			*B.* In Large Globe.		
	p_1	701 mm.			685 mm.		
	p_2	1018 ,,			1187 ,,		
	p_2/p_1	1·45			1·73		
Percentage Composition of Gaseous Products.	CO_2	4·20			3·40		
	CO	34·80			36·10		
	C_2H_2	5·00	7·65		0·15		
	C_2H_4	2·65					
	CH_4	8·85			7·25		
	H_2	44·50			53·05		
		C.	H.	O.	C.	H.	O.
Original mixture		694	1041	354	678	1017	346
Gaseous products		643	738	220	558	805	255
Difference		51	303	134	120	212	91
Per cent. Difference		7·6	29	37·8	18	20	27·5

(3) *Detonation and Explosion at High Pressure.* The ‘ hydroxylation ’ theory having proved capable of explaining the facts observed when the $C_2H_6 + O_2$ mixture was inflamed (*i.e.* under ordinary flame conditions), it remained to study its behaviour under the extreme conditions of ‘ detonation ’ and explosion at high initial pressures respectively.

(*a*) It is not easy to set up ‘ detonation ’ in such a mixture ($C_2H_6 = 50·25$, $O_2 = 49·75$ per cent.), but eventually, by filling the leaden coil (Fig. 148) with it at 17° C. and 1180 mm. and then raising the temperature to 100° C., by heating the surrounding water to boiling point—the firing piece having previously been charged up with electrolytic gas to 3 atmospheres, and the connecting tap *C* opened immediately before firing—a very violent explosion was set up. A heavy sound indicated the setting up of ‘ detonation ’ in the electrolytic gas, and at the same instant a sharp metallic click at the far end of the coil shewed that the explosion wave had been propagated through the $C_2H_6 + O_2$ mixture in it. So violent was the explosion that the lead coil, though a specially strong one, was permanently enlarged throughout its whole length, its total volume increasing from 3300 to 3900 c.c. Making due allowance for this volume-increase, and for the fact that the cooled products at the end of the experiment filled both the coil and the firing-piece, the ‘corrected’ pressure of the cold products at 17° C. was 2240 mm., so that the p_2/p_1 ratio=1·90. A subsequent examination of the coil shewed that its diameter had been increased by 2·5 to 3·5 mm. throughout a length of 19 ft. 4 ins. out of a total of 20 ft., whilst at the end farthest from the firing piece it had been bulged out into a pear-shaped form, so violent had been the explosion. Moreover, in another similar experiment, so arranged that an approximate timing of the explosion could be made, it was impossible to distinguish between the moment of firing and that of the flame reaching the farthest end, where a stout test-tube attached to it was shattered with a deafening report accompanied by a black cloud of carbon. Indeed the whole thing seemed to have been instantaneous, and there could be no doubt about ‘detonation’ having been set up.

(*b*) A similar equimolecular $(C_2H_6+O_2)$ mixture was subsequently exploded at an initial pressure of 25·21 atmospheres in the cylindrical bomb *A* (Fig. 149), the explosion chamber of which was 8 inches long by 1 inch in diameter. A sharp metallic ‘click’ was heard; carbon was liberated, steam condensed on cooling, and the ‘corrected’ p_2/p_1 ratio was 2·05. Subsequent analysis shews that some 3 per cent. of the original carbon had been liberated, and 12 per cent. of the original oxygen condensed out as water.

TABLE CVIII.—RESULTS OF EXPLOSION OF AN EQUIMOLECULAR MIXTURE OF ETHANE AND OXYGEN UNDER HIGH PRESSURES

		A. Detonation in Lead Coil.			*B.* Explosion in Steel Bomb.		
	p_1	1180 mm.			25·2 atms.		
	p_2	2240 ,,			51·7 ,,		
	p_2/p_1	1·90			2·05		
Percentage Composition of Gaseous Products	CO_2	1·80			2·6		
	CO	39·10			37·7		
	C_2H_2	0·90 } 1·40			*nil*		
	C_2H_4	0·50					
	CH_4	7·70			7·0		
	H_2	50·00			52·7		
		C.	H.	O.	C.	H.	O.
Original mixture - -		1186	1779	587 mm.	25·35	38·0	12·55 atms.
Gaseous products - -		1151	1507	488 ,,	24·50	34·6	11·05 ,,
Difference - -		35	272	99 ,,	0·85	3·4	1·5
Per cent. Difference		3	15	17	3·4	9	12·0

The results of these experiments are analysed in Table CVIII, and should be compared with those obtained when the same mixture was ‘inflamed’ in the long glass tube and the large globe, respectively. To facilitate such comparison the results of the four experiments are all summarised in Table CIX.

TABLE CIX.—EXPLOSION OF $C_2H_6+O_2$ MIXTURE

Experimental Conditions.	Inflammation in		Detonation in Lead Coil. 20 Metres long. 36 mm. internal diameter. Volume = 3100 c.c.	Explosion in Steel Bomb under High Initial Pressure.
	Long Glass Tube. 1·5 metre long. 20 mm. internal diameter. Volume = 470 c.c. Area of Walls = 940 cm².	*Glass Globe.* Internal Diameter = 8·5 cm. Volume = 320 c.c. Area of Walls = 226 cm².		
	mm.	mm.	mm.	Atms.
p_1	701	685	1180	25·2
p_2	1018	1187	2240	51·7
p_2/p_1	1·45	1·73	1·90	2·05
Percentage Composition of Gaseous Products. CO_2	4·20	3·40	1·80	2·6
CO	34·80	36·10	39·10	37·7
C_2H_2	5·00 } 7·65	0·15	0·90 }	*nil*
C_2H_4	2·65 }		0·50 }	
CH_4	8·85	7·25	7·70	7·0
H_2	44·50	53·05	50·00	52·7
Percentage of original carbon deposited	7·6	18	3	3·4
Percentage of original oxygen appearing as H_2O, etc., in condensable products	37·8	27·5	17	12·0
Remarks	Luminous flame travelled at approximately 0·5 metre per second. Each successive layer of the burning gas remained incandescent $\frac{1}{20}$ to $\frac{1}{30}$ second. Products gave strong aldehydic reaction; much steam condensed on cooling.	Lurid flame filled the globe and was of longer duration than in (*a*). Products gave faint aldehydic reaction, and steam condensed on cooling.	Coil filled cold; then its temperature was raised to 100° C. before the mixture was detonated; afterwards apparatus cooled by immersion in cold water. Explosion very violent, and practically instantaneous.	Sharp Metallic Click.

It is thus seen that, even under the extreme conditions of ‘detonation’ and the high-pressure explosion, carbon was deposited, water condensed, and much methane appeared in the products. Naturally much less steam survived under such conditions than under those of ordinary inflammation, and it is interesting to observe that the ‘high pressure explosion’ was less favourable to steam survival than in the detonation at a much lower pressure. Moreover, the ‘high pressure explosion’ was the only one in which no trace of either acetylene or ethylene could be found in the final products, a circumstance which also testifies to the extreme conditions which must have prevailed in it.

H. B. Dixon subsequently found the rate of detonation of the $C_2H_6+O_2$ mixture to be 2180 metres per sec., and the cooled gaseous products to contain $CO_2=0{\cdot}75$, $CO=38{\cdot}55$, C_2H_2 and $C_2H_4=1{\cdot}10$, $CH_4=8{\cdot}15$, and $H_2=51{\cdot}10$ per cent., some carbon being deposited and steam condensed, the ratio p_2/p_1 being about 2·0. He afterwards expressed the opinion that in the explosion-wave “The ethane is not burnt wholly to carbon monoxide and hydrogen, but appears to form (as Professor Bone has shewn at lower temperatures) acetaldehyde and steam, the acetaldehyde yielding methane and carbon monoxide.” * And, in a recent private communication he agreed that probably the main (though not necessarily the only) primary burning was to aldehyde and steam.† So we think that the facts observed in both the ‘detonation’ and ‘inflammation’ of the said mixture are best explained on the ‘hydroxylation’ theory.

Experiments on Ethylene and Higher Olefines

In a long series of ‘sealed-bulb’ experiments with olefines (ethylene, propylene and butylenes), as well as with trimethylene, it was found that, whereas mixtures containing proportions of oxygen corresponding with

$$C_nH_{2n}+\frac{n}{2}O_2$$

yield on explosion mainly carbonic oxide and hydrogen, without any separation of carbon, or material steam formation, *as though* a preferential combustion had occurred, thus :

$$C_nH_{2n}+\frac{n}{2}O_2=nCO+nH_2,$$

---

* Presidential Address to the Chemical Society, *Trans. Chem. Soc.* 97 (1910), p. 665.

† Professor Dixon expressed himself as follows : “ I think the main reaction taking place in the explosion-wave is the one I understand you adopt :

$$C_2H_6+O_2=CH_3\cdot CHO+H_2O,$$
$$CH_3\cdot CHO=CH_4+CO.$$

But I would not exclude the other reaction as impossible because this is the main one. I imagine the oxygen molecules running into the ethane molecules at all sorts of angles with regard to the ‘axis of orientation’ of the ethane and therefore possibly uniting with the two carbons direct.”

yet on reducing the proportion of oxygen below such ratio both carbon and steam as well as aldehyde vapours appeared in the products ; *indeed the more the proportion of oxygen in the mixture fired was reduced below such ratio the more of it appeared as water in the cooled products.* This remarkable circumstance, whilst quite consistent with the hydroxylation theory, was fatal to that of the preferential combustion of carbon, which accordingly has been abandoned. Also, it can hardly be explained on the supposition of the initial oxidation-product being a ‘ peroxide ’ rather than a mono-hydroxy compound.

In order to bring these crucially important results clearly before the reader’s mind, they have been summarised in Tables CX and CXI, respectively, which shew (i) those obtained when the $C_nH_{2n}+\frac{n}{2}O_2$ mixtures were exploded, and (ii) the effect upon steam formation, etc. of progressively reducing the oxygen supply below the said ratio.

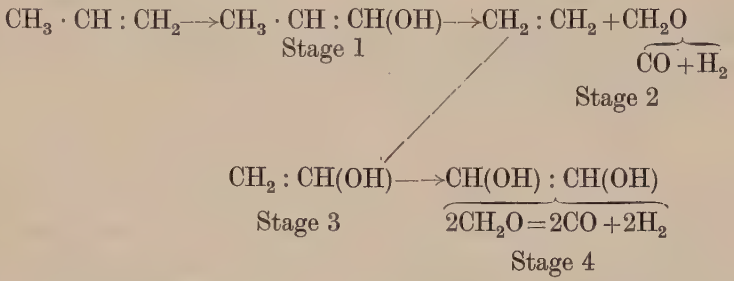
TABLE CX.—INFLAMMATION OF $C_nH_{2n}+\frac{n}{2}O_2$ MIXTURES IN SEALED GLASS BULBS

Hydrocarbon.		Ethylene.	Propylene.	Trimethylene.	Butylenes.	
Original mixture		$C_2H_4+O_2$	$C_3H_6+1\frac{1}{2}O_2$	$C_3H_6+1\frac{1}{2}O_2$	$C_4H_8+2O_2$	
					n.	iso-
	p_1	545·3 mm.	563·0 mm.	552·7 mm.	479·0 mm.	438·0 mm.
	p_2	1053·5 mm.	1244·0 mm.	1186·7 mm.	1169·0 mm.	982·5 mm.
	p_2/p_1	1·93	2·20	2·15	2·43	2·20
Percentage Composition of Gaseous Products	CO_2	0·3	0·1	0·60	0·90	1·40
	CO	50·0	50·9	49·30	50·50	50·20
	H_2	48·0	46·5	48·80	46·35	43·50
	CH_4	1·7	1·5	0·45	1·60	3·00
	$C_2H_2+C_2H_4$ etc.	*nil*	1·0	0·85	0·65	1·90
Units in		C. H. O.	C. H. O.	C. H. O.	C. H. O.	C. H. O.
Original mixture		545 545 272	675 675 338	663 663 331	630 630 322	584 584 292
Final products		547 541 267	677 634 318	617 610 299	634 590 305	574 515 260
Difference		Practically *nil*	— 41 20	46 53 32	— 40 17	10 69 32
Remarks		(1) There was no separation of carbon in any of the experiments. (2) In the case of the experiment with trimethylene, the products gave a distinct aldehydic reaction. (3) Except with the $C_2H_4+O_2$ mixture, a *slight* condensation of steam was usually observed.				

TABLE CXI.—INFLAMMATION OF OLEFINE-OXYGEN MIXTURES CONTAINING LESS OXYGEN THAN $C_nH_{2n} + \frac{n}{2} O_2$

Hydrocarbon.		Ethylene.	Propylene.	Trimethylene.	*n*-Butylene.	*n*-Butylene.	iso-Butylene.
Original mixture - -		$\underbrace{3C_2H_4 + O_2}$ $C_2H_4 = 59{\cdot}65$ $O_2 = 40{\cdot}35$	$\underbrace{C_3H_6 + 1\frac{1}{4}O_2}$ $C_3H_6 = 45{\cdot}0$ $O_2 = 55{\cdot}0$	$\underbrace{C_3H_6 + O_2}$ $C_3H_6 = 48{\cdot}15$ $O_2 = 51{\cdot}85$	$\underbrace{C_4H_8 + 1\frac{1}{2}O_2}$ $C_4H_8 = 39{\cdot}6$ $O_2 = 60{\cdot}4$	$\underbrace{C_4H_8 + 1\frac{1}{7}O_2}$ $C_4H_8 = 46{\cdot}6$ $O_2 = 53{\cdot}4$	$\underbrace{C_4H_8 + 1\frac{1}{2}O_2}$ $C_4H_8 = 39{\cdot}7$ $O_2 = 60{\cdot}3$
	p_1	562·3 mm.	682·0 mm.	563·7 mm.	574·0	487·4 mm.	606·5
	p_2	816·4 mm.	1213·0 mm.	936·3 mm.	1094·0	904·0 mm.	1107·6
	p_2/p_1	1·451	1·78	1·66	1·90	1·85	1·83
Percentage Composition of Gaseous Products	CO_2	2·50	3·20	2·8	3·50	1·80	3·85
	CO	37·20	43·05	40·5	41·40	37·90	39·85
	$C_2H_2 + C_2H_4$	6·40	4·90	5·9	4·75	8·20	5·90
	CH_4	6·50	6·90	6·3	7·55	15·20	8·10
	H_2	47·40	41·95	44·5	42·80	36·90	42·30
Units in		C. H. O.	C. H. O.	C. H. O.	C. H. O.	C. H. O.	C. H. O.
Original mixture - -		670 670 227	918 918 376	814 814 292	899 899 347	909 909 260	958 958 363
Gaseous products - -		482 572 172	763 766 300	575 618 216	678 713 265	644 720 187	702 744 262
Difference - -		188 98 55	155 152 76	239 196 76	221 186 82	265 189 73	256 214 101
Percentage of the original O_2 appeared in condensed products - - -		24·4	20	26	23·6	29	27·5
Remarks - -		The products in all these experiments gave a very distinct aldehyde reaction.					

It seemed as though that in an oxygen supply sufficient to burn an olefine entirely to formaldehyde, *i.e.* when the combustible mixture has the composition $C_2H_{2n}+\frac{n}{2}O_2$, the combustion involves successive elimination of that substance, which then decomposes into carbonic oxide and hydrogen, without any separation of carbon or steam formation. Thus, in the case of propylene, the process may perhaps be crudely represented somewhat as follows :



$$CH_3\cdot CH:CH_2 \longrightarrow \underset{\text{Stage 1}}{CH_3\cdot CH:CH(OH)} \longrightarrow CH_2:CH_2+\underset{\substack{\overbrace{CO+H_2}\\ \text{Stage 2}}}{CH_2O}$$

$$\underset{\text{Stage 3}}{CH_2:CH(OH)} \longrightarrow \underset{\text{Stage 4}}{\underset{\overbrace{2CH_2O=2CO+2H_2}}{CH(OH):CH(OH)}}$$

With a more limited supply of oxygen, say two-thirds of that required for the above scheme, the process would go as far as Stage 3 ; there would then be no more oxygen left, so that the $CH_2:CH(OH)$ would break down, when acetylene and steam, or carbon, hydrogen and steam, as well as methane would probably result.

At any rate, it can be truly said that whenever an olefine oxygen mixture of the composition $C_nH_{2n}+\frac{n}{2}O_2$ is exploded, the products are identical with those (namely $CO+H_2$) yielded when formaldehyde thermally decomposes at high temperatures. This gives the process the *appearance* of a preferential combustion of carbon, which, however, it is not, because whenever the amount of oxygen present is materially reduced below the aforesaid proportion, the products (carbon, steam, aldehyde, acetylene, methane, etc.) are such as might be expected to arise by the thermal decomposition of hydroxylated molecules of the type

$$H_2C:CH(OH).$$

Experiments on Acetylene

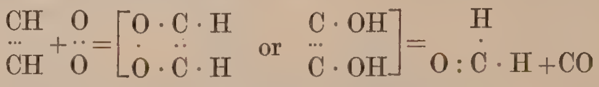
The following typical experiment in which an exactly equimolecular mixture of acetylene and oxygen was exploded in a sealed glass bulb at an initial pressure of 352 mm. may be quoted. The explosion was quite sharp with a non-luminous flame ; there was no separation of carbon nor any condensation of moisture when the system cooled, the products consisting almost entirely of carbonic oxide and hydrogen, as shewn below :

$$p_1=352 \text{ mm.}, \; p_2=508 \text{ mm.}, \; p_2/p_1=1{\cdot}44.$$

Gaseous Products $CO_2 = 0{\cdot}75$, $CO = 67{\cdot}10$, $H_2 = 30{\cdot}60$, and $CH_4 = 1{\cdot}55$ per cent.

	C.	H.	O.
Units in original mixture - - -	352	176	176
Units in gaseous products - -	352	171	175

It is perhaps rather difficult to bring such a strongly endothermic gas as acetylene into a general view of explosive combustion, for indeed some difference in its behaviour might be looked for, as compared with that of either ethane or ethylene. Experiments on the slow combustion of equimolecular acetylene-oxygen mixtures shewed a considerable formaldehyde formation, as though its mechanism had been



$$\begin{matrix}\mathrm{CH}\\ \cdots\\ \mathrm{CH}\end{matrix} + \begin{matrix}\mathrm{O}\\ \cdot\cdot\\ \mathrm{O}\end{matrix} = \left[\begin{matrix}\mathrm{O \cdot C \cdot H}\\ \cdot\quad\cdot\cdot\quad\\ \mathrm{O \cdot C \cdot H}\end{matrix} \quad \text{or} \quad \begin{matrix}\mathrm{C \cdot OH}\\ \cdots\quad\\ \mathrm{C \cdot OH}\end{matrix}\right] = \mathrm{O : \overset{\overset{H}{\cdot}}{C} \cdot H + CO}$$

And when the same mixture is exploded, the cooled products are simply $2CO + H_2$, as though in the flame the formaldehyde had been resolved into $CO + H_2$, the normal products of its thermal decomposition. Hence, there is no difficulty in explaining its explosive combustion on the supposition that it follows the course of its slow combustion. In an experiment in which a $2C_2H_2 + O_2$ mixture was inflamed, the products mainly consisted of carbon, carbonic oxide, and hydrogen together with a little methane, no steam at all being produced. It seemed as though, in such circumstances, half the acetylene was burnt in accordance with the foregoing scheme, the remainder being simultaneously resolved by heat into its elements, together with some methane.

The Combustion of Paraffins and Olefines Contrasted

A series of comparative experiments with ethane, propane, and butanes, on the one hand, and with ethylene, propylene and butylenes on the other, shewed that, whereas mixtures of olefines and oxygen of the composition $C_nH_{2n} + \frac{n}{2}O_2$ yield almost entirely carbonic oxide and hydrogen on explosion, without any separation of carbon, or material amount of steam, similar mixtures of the corresponding paraffins and oxygen, *i.e.*

$$C_nH_{2n+2} + \frac{n}{2}O_2$$

always yield carbon, oxides of carbon, methane, hydrogen and steam, all in considerable quantities. This striking difference in the outward behaviour of the two classes of hydrocarbons, whilst fatal to any idea of a preferential combustion of carbon, is just what might be predicted by the 'hydroxylation' theory. The case of such olefine-oxygen mixtures having already been dealt with, it need only be said that the corresponding paraffin-oxygen mixtures might be expected to burn in stages such as,

$$CH_3 \cdot CH_2 \cdot CH_3 \rightarrow CH_3 \cdot CH_2 \cdot CH_2OH \rightarrow \underbrace{CH_3 \cdot CH_2 \cdot CH(OH)_2}_{CH_3 \cdot CH_2 \cdot CHO + H_2O}, \text{ etc.}$$

The aldehyde so formed decomposing into CO and the next lower paraffin, which latter would then burn in similar manner. Alternatively, the primary oxidation product $C_nH_{2n+1} \cdot OH$ might decompose into $C_nH_{2n} + H_2O$, the olefine then burning in its own peculiar way. No doubt the explosive combustion of a long-chain paraffin is a very complex process, not easily represented by rigid schemes and equations, but essentially it may be regarded as involving the primary formation of ‘ hydroxylated ’ (or possibly ‘ oxygenated ’) molecules much on some such lines as here suggested.

For details concerning the behaviour of propane, butanes and the corresponding olefines, which have an important bearing upon the theoretical views advanced in this chapter, the original papers should be consulted.*

So far in this chapter we have mainly considered the behaviour of certain typical hydrocarbons when exploded with considerable defect of oxygen, because it is only in such circumstances that we can obtain trustworthy evidence of what are the primary interactions.

The secondary reactions which may supervene upon the primary oxidation are doubtless very complex, comprising as they do secondary decompositions of hydroxylated molecules, aldehydes, hydrocarbons, further oxidations of such products, interactions between carbon and steam and in the reversible system $CO + OH_2 \rightleftharpoons CO_2 + H_2$, as the gaseous medium cools down from the maximum temperature attained in the explosion.

The thermal decomposition of alcohols and aldehydes has already been dealt with, and those of the simpler hydrocarbons will be considered in a future chapter. All of these are very important, especially from the point of view of the luminosity of hydrocarbon flames.

There can be no doubt that whenever both carbon and steam are formed, or are present simultaneously, in hydrocarbon flames, they will interact ($C + OH_2 = CO + H_2$) during the cooling period more or less according to the subsequent rate of cooling. In general, the hotter the flame, and the slower the rate of cooling, the greater the chance of steam being unburnt by carbon. This point is well brought out by the experiments upon the explosion of a $C_2H_6 + O_2$ mixture detailed in Table CIX, and need not be laboured.

Equally important is the operation of the reversible reaction

$$CO + OH_2 \rightleftharpoons CO_2 + H_2$$

during the cooling period; for, if the tabulated results of the numerous experiments detailed in this chapter be carefully considered, it will be found that whenever the 'hydroxylation' theory would anticipate the simultaneous formation or presence of steam and carbonic oxide at an early stage in the combustion (as for instance in the case of CH_4+O_2, $C_2H_6+O_2$, $3C_2H_4+2O_2$, etc. mixtures), the cooled products always contained substantial quantities of carbon dioxide. On the other hand, in cases (*e.g.* $C_2H_4+O_2$, $C_3H_6+1\frac{1}{2}O_2$, $C_2H_2+O_2$, etc. mixtures) where there was no such expectation, the cooled products contained little or no carbon dioxide, a very significant circumstance.

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* Bone and Drugman, *loc. cit.*

In Chapter XXV (pp. 322-3) reference was made to the work of G. W. Andrew, who shewed that whenever hydrogen, steam and the oxides of carbon, produced during the incomplete explosive combustion of hydrocarbons, are allowed freely to interact in absence of carbon during the cooling period, the ratio $\frac{CO \times OH_2}{CO_2 \times H_2}$ in the cold products usually comes out near 4·0, as though the equilibrium adjusts itself automatically with the falling temperature until a point somewhere between 1400 and 1600° C. is reached, when it 'freezes out.'

Concluding Remarks

From what has been said in this and the preceding chapter, it may be claimed that, whilst the two older theories of 'preferential combustion,' whether of hydrogen or of carbon, are quite incapable of explaining the facts, as now known, the 'hydroxylation' theory advanced more than twenty years ago can still look them squarely in the face. It should, however, not be interpreted or applied too rigidly, because doubtless in the long run the steady accumulation of new facts will necessitate some modifications, and it would be unphilosophical to regard it as more than a serviceable tool for accomplishing further advances. It certainly affords what we believe to be a true explanation of slow combustion; and, as regards the rest, we would repeat what one of us said when summing up the position in 1908, namely, that whilst the sequence of changes observed in slow combustion may not be exactly reproduced in flames, "the immediate result of the initial encounter between hydrocarbon and oxygen is probably much the same in the two cases, namely, the formation of a 'hydroxylated' or 'oxygenated' molecule. At the higher temperatures of flames, secondary thermal decompositions and interactions undoubtedly come into operation at an earlier stage, and play a more important role, than in slow combustion; they do not, however, precede the onslaught of the oxygen upon the hydrocarbon but arise in consequence of it." *

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* W. A. Bone's Discourse on "Explosive Combustion with Special Reference to that of Hydrocarbons," at the Royal Institution, 28th February, 1908.

CHAPTER XXXI

THE RELATIVE COMBUSTIBILITIES OF HYDROCARBONS, HYDROGEN, AND CARBONIC OXIDE IN FLAMES

In Chapter VI it was related how in 1856 H. Landolt had endeavoured to determine the order of the combustibilities of the principal constituents of coal gas, whereby he arrived at the conclusion that hydrogen is the most combustible of all, methane following next, and the heavy hydrocarbons last of all. It is now realised, however, that in his experiments the real flame reactions had been masked by the catalytic combustion induced by the way in which the products had been drawn off for analysis from the middle of the flame through a narrow platinum tube, which would become red-hot during the operation. It was also shewn how, in 1861, on exploding a mixture of ethylene and electrolytic gas, Kersten had found that the hydrocarbon had burnt preferentially to the hydrogen.

In the course of the researches of W. A. Bone and his collaborators much new evidence was obtained of hydrocarbons having a much greater affinity than hydrogen for oxygen in flames, and this important aspect of our subject will now be reviewed.

The first experiments made by Bone and Drugman in this connection * were undertaken to test an idea put forward by W. Misteli in 1905 † that in hydrocarbon flames generally the oxygen does not react with the hydrocarbons as such, but only with their decomposition products, which he supposed would be mainly carbon and hydrogen in such circumstances. He supposed that, on exploding mixtures of electrolytic gas with either acetylene or ethylene, the whole of the hydrocarbon is initially resolved into its elements. The oxygen in the system would then react with the carbon and hydrogen present, the carbon burning preferentially.

Such a view, being contrary to that embodied in the 'hydroxylation' theory, Bone and Drugman decided to test the matter experimentally in a way which would be decisive as between the two ideas. And for such purpose they exploded mixtures of the composition $C_2H_6 + O_2$, $C_2H_4 + H_2 + O_2$,

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* *Trans. Chem. Soc.* 89 (1906), pp. 669–671.

† *Journ. Gasbeleuchtung*, 48 (1905), pp. 802–804.

and $C_2H_2+2H_2+O_2$—that is to say all containing the same relative proportions of carbon, hydrogen and oxygen—because, if Misteli's view is correct, such mixtures yield on explosion much the same products.

On exploding the mixtures in question in sealed glass bulbs, however, it was immediately seen that Misteli's view was not upheld, as the following tabulated results will shew :

TABLE C.—RESULTS OF THE EXPLOSION OF THE MIXTURES
$C_2H_6+O_2$, $C_2H_4+H_2+O_2$ AND $C_2H_2+2H_2+O_2$
(BONE AND DRUGMAN)

Original mixture.	$C_2H_6+O_2$.			$C_2H_4+H_2+O_2$.			$C_2H_2+2H_2+O_2$.		
p_1	746 mm.			503 mm.			534 mm.		
p_2	1148 mm.			750 mm.			653 mm.		
p_2/p_1	1·54			1·49			1·22		
Percentage composition of gaseous products: CO_2	4·20			0·35			0·2		
CO	33·55			39·60			39·8		
$C_2H_2+C_2H_4$	2·75			1·25			*nil*		
CH_4	10·85			3·65			0·2		
H_2	48·60			55·15			59·8		
	C	H	O	C	H	O	C	H	O
Original mixture	746	1119	376	341	505	168	267	400	133
Gaseous products	621	854	241	346	478	151	262	394	131
Difference	125	265	135	—	27	17	Negligible.		

For, whereas the equimolecular ethane-oxygen mixture yielded free carbon, oxides of carbon, methane, hydrogen and steam, all in considerable proportions, the other two mixtures behaved quite differently, no carbon being liberated and little or no steam formed, the products consisting almost entirely of carbonic oxide and hydrogen.

It is indeed remarkable that on exploding such a mixture as

$$C_2H_4+H_2+O_2$$

no carbon at all is deposited, and only about 10 per cent. of the original oxygen appears as steam in the final products ; and still more so that in the explosion of a $C_2H_2+2H_2+O_2$ mixture neither separation of carbon nor any steam formation can be detected. Apparently in such cases, the hydrocarbon gets most, or even all, of the oxygen, the hydrogen being left out in the cold. Such striking results naturally lead to the conclusion that the affinities of the said hydrocarbons far exceed that of hydrogen for oxygen in flames.

Some years later W. A. Bone, in conjunction with H. Davies and H. H. Gray, carried the matter a step further * by exploding a mixture of methane and electrolytic gas of the composition $CH_4 + O_2 + 2H_2$ at high initial pressure in steel bombs, one of which (*A*) had a cylindrical explosion chamber 8 inches long by 1 inch diameter, and the other (*B*) a spherical one 3 inches in diameter. This particular explosive mixture was chosen for the experiments because, whilst the relationship between the methane and oxygen in it was equimolecular corresponding with the supposition that the primary oxidation of methane in explosions usually involves a direct transition from $CH_4 + O_2$ to $CH_2(OH)_2$, the hydrogen and oxygen were present in the proportion in which they would burn to steam. And the experimental results were interpreted on the supposition that the oxygen would interact with the two combustible gases as follows:

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* *Phil. Trans.* A. 215 (1915), pp. 296 to 308.

$$CH_2(OH)_2 \xleftarrow{\textit{forming}} CH_4 \xleftarrow{\textit{with}} O_2 \xrightarrow{\textit{with}} 2H_2 \xrightarrow{\textit{forming}} H_2O$$

$$\overbrace{H_2 : C :}\overbrace{O + H_2O}$$

$$\overbrace{CO + H_2}$$

In other words, it was supposed that the division of oxygen between the two combustible gases would occur in accordance with the principle of mass action.

Preliminary trials having proved that no carbon was ever deposited during such explosions, it was easy to determine what percentage of the original methane had been burnt by carefully ascertaining what proportion of it remained intact in the final products. Then, assuming the methane burnt to have reacted with its own volume of oxygen, the distribution of the oxygen as between methane and hydrogen in the explosion was deduced. Whatever view may be taken of such assumption, however, the experiments did shew the relative proportions of methane actually burnt and unburnt in each explosion. These varied somewhat with the surface volume ratio of the explosion chamber, which is what might be expected seeing that the maximum temperature of the explosion would also be affected thereby. Thus it was found:

TABLE CI.—RESULTS OF EXPLOSIONS OF A $CH_4 + O_2 + 2H_2$ MIXTURE (BONE, DAVIES AND GRAY)

-	Bomb *A*.			Bomb *B*.		
Initial pressure (atms.) -	18·33	19·62	48·85	17·12	18·31	21·12
Final pressure of cold products (atms.) -	18·25	19·45	48·15	17·15	18·12	21·08
Percentage of original methane remaining unburnt - - -	4·3	5·25	4·4	3·1	2·8	2·80
Calculated O_2-distribution to CH_4	95·7	94·75	95·6	96·9	97·2	97·20
Calculated O_2-distribution to H_2 -	4·3	5·25	4·4	3·1	2·8	2·80

From these results it is clear that the methane got by far the lion's share of the oxygen. Indeed, on the assumption referred to, its affinity would appear to be something like twenty to thirty times stronger than that of hydrogen for oxygen in explosion flames. And, although such figures should not be overstressed, they may be regarded as revealing the *order* of the difference.

Similar experiments were also made in Bomb *B* with a mixture of the composition CH_4+O_2+2CO. Here again, no carbon was deposited on explosion, and the methane captured by far the most of the oxygen, as the following results shew :

TABLE CII.—RESULTS OF EXPLOSIONS OF CH_4+O_2+2CO MIXTURE IN BOMB *B* (BONE, DAVIES AND GRAY)

Initial pressure (atms.)	20·90	19·44
Final pressure of cold products (atms.)	22·66	21·33
Percentage of original methane remaining unburnt	5·1	4·3
Calculated distribution of O_2 to CH_4	94·9	95·7
Calculated distribution of O_2 to CO	5·1	4·3

R. V. Wheeler has objected to our interpretation of the foregoing results, and would have us believe that " when a mixture of methane, hydrogen and oxygen, the oxygen being in defect, is inflamed, the methane must of necessity combine with the major portion of the oxygen because the methane-oxygen association that is required to yield the same speed of flame as the hydrogen-oxygen association is the richer in oxygen." * Unfortunately, however, for his argument, the supposed 'flame speed law,' on which it depended, completely broke down when tested with methane-hydrogen-oxygen mixtures, and it may be ruled out.

The matter may be followed a step further, for when a series of mixtures of the composition $CH_4+O_2+xH_2$, where $x=2$, 4, 6 and 8, were exploded at high pressures in each of the two bombs referred to, the following significant results were obtained :

TABLE CIII.—MEAN RESULTS OF EXPLOSIONS OF $CH_4+O_2+xH_2$ MIXTURES IN BOMBS *A* AND *B* (BONE, DAVIES AND GRAY)

x.	2.	4.	6.	8.
Percentage of the original methane unburnt - Bomb *A*	4·66	19·0	45·1	68·6
Percentage of the original methane unburnt - Bomb *B*	2·9	9·0	27·4	—

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* *Trans. Chem. Soc.* 121 (1922), p. 379.

In other words, *the influence of successive increases in* x, *i.e. in the volume ratio of* H_2 *to* CH_4 *in the mixture exploded, upon the percentage of the methane unburnt in the explosion was as nearly as possible proportional to* x^2, a result which suggests that in explosion flames hydrogen is burnt to steam as the result of trimolecular impacts.

From the facts recorded in this chapter it would appear that when mixtures such as $CH_4 + O_2 + 2H_2$, $C_2H_4 + O_2 + H_2$, or $C_2H_2 + O_2 + 2H_2$ are exploded, there ensues a competition between the hydrocarbon and hydrogen for the limited supply of oxygen resulting in the hydrocarbon getting nearly all of it; and we think the most natural interpretation of such results is that the affinity of the hydrocarbon is far greater than that of hydrogen for oxygen in flames. Alternatively, out of consideration for those whose feelings may be shocked by the use of the word ‘affinity’ in such connection, we might put it differently by saying that the hydrocarbons in question are in fact much more combustible than hydrogen in flames.

CHAPTER XXXII

THE THERMAL DECOMPOSITIONS OF HYDROCARBONS AS A CAUSE OF THE LUMINOSITIES OF THEIR FLAMES

In Chapter IV it was stated that Davy attributed the luminosity of hydrocarbon flames to the presence of incandescent carbon particles, which he said " might be owing to a decomposition of a part of the gas towards the interior of the flame where the air was in smallest quantity." And in Chapter XVII it was shewn that the ' incandescent carbon ' theory had been substantiated, and is now generally accepted. So far, however, nothing has been said as to how the carbon particles arise in hydrocarbon flames, except that the former notion of their being due to ' preferential combustion of hydrogen ' has proved untenable.

From what was said in the preceding chapter concerning the thermal decompositions of alcohols and aldehydes, one probable cause of carbon separation in flames has been indicated. It remains, however, to consider how, and in what circumstances, the hydrocarbons themselves might decompose " toward the interior of the flame where the air was in smallest quantity." And, in doing so, the reader should bear in mind that, in general, the rates of oxidation of hydrocarbons in flames exceed those of their thermal decompositions.

In this connection we may quote the view expressed some years ago by A. Smithells when he said " it may be affirmed that, generally speaking, hydrocarbons, subjected to a high temperature, deposit solid carbon. It would appear, therefore, that the separation of carbon in a flame might be adequately explained by the fact that the unburned hydrocarbon within the burning sheath of the flame is highly heated by the burning parts. . . . At the same time, the experiments of Bone would lead us to be cautious in denying that in some cases the chemical processes might contribute to the separation of carbon." *

It was Marchand's experimental study in 1839 of the thermal decomposition of ethylene at bright-red heat which first set the ball rolling. He

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* Article on " Flame," in Thorpe's *Dictionary of Applied Chemistry*, 1912 ed., vol. ii. p. 576.

found that large quantities of carbon and methane were obtained, and concluded that the process could be represented by the simple equation:*

$$C_2H_4=C+CH_4.$$

This conception long served as a possible explanation of luminosity of hydrocarbon flames, but eventually it became untenable, because modern research has proved the matter to be much more complex than was then supposed.

During the years 1863–9 Berthelot made a comprehensive study of the decomposition of hydrocarbons at high temperatures.† He had just previously rediscovered acetylene, whose wonderful properties he was the first to explore, and had demonstrated its synthesis in the electric arc between carbon poles in an atmosphere of hydrogen. He assigned to it a capital *rôle* in such processes, describing it as "*le produit ultime des décompositions pyrogenées . . . générateur fondamental des carbures pyrogenées.*"

As the result of his researches he propounded the doctrine that no hydrocarbon (not even acetylene) is ever directly resolved by heat into its elements, but that its primary decomposition always involves either a polymerisation (*e.g.* acetylene to benzene) or a coalition of two or more molecules to form a denser one with elimination of hydrogen; also, that it is by the further mutual coalitions of such dense hydrocarbon molecules, with the elimination of hydrogen at each stage, that something very nearly carbon is at length obtained as the final product of the decomposition of an extremely complex molecular aggregate. Thus he wrote: "*que la décomposition immédiate d'un carbure d'hydrogène ne répond pas à sa résolution en éléments, mais à sa transformation en polymères, ou en carbures plus condensés avec perte d'hydrogène.*" ‡ This theory, according to which on being heated the molecules of hydrocarbons undergo progressive coalescence with elimination of hydrogen until ultimately a dense molecule is left containing so negligible a proportion of hydrogen that it may be regarded as carbon, gained many adherents and for a long time held the field; but it had to be abandoned towards the end of last century because of its incompatibility with the results of new experiments.

In 1892 V. B. Lewes put forward a theory postulating that the formation of acetylene and its subsequent decomposition are the essential cause of the luminosity in hydrocarbon flames. § He agreed with Berthelot in assigning a pivotal rôle to acetylene, and in regarding it as a primary and principal product of the thermal decompositions of methane, ethylene, etc., which he represented as follows :

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* *Jour. prak. Chem.* 36, p. 478.

† *Ann. Chim. Phys.* 1863 (iii.), 67, 53; 1866 (iv.), 413, 455; 1867 (iv.), 125, 122; 1869 (iv.), 16, 143, 148, 153, 162.

‡ *Amm. Chem. Phys.* 1866 (iv.), 9, p. 471.

§ *Trans. Chem. Soc.* 69 (1892), 322; *Proc. Roy. Soc.* 55 (1894), 90; 57 (1895), pp. 344 350.

$$2CH_4 = C_2H_2 + 3H_2,$$
$$3C_2H_4 = 2C_2H_2 + 2CH_4.$$

He differed from Berthelot, however, in considering acetylene capable of direct decomposition into its elements at high temperatures with explosive effect, owing to its strong endothermic character. And here he was undoubtedly right. His theory of the luminosity of hydrocarbon flames generally was based upon the belief that in the inner zone, under the influence of radiant heat from the outer envelope, hydrocarbons generally are largely converted into acetylene, which at the still higher temperatures of the luminous region is resolved explosively into its elements, the liberated particles being raised to a much higher temperature than that of the surrounding flame, consequent upon the sudden disengagement of the energy locked up within the acetylene molecules.

Whilst it is quite likely that such an explanation may apply to the highly luminous acetylene flame, and possibly even to an ethylene flame, it seems untenable as a theory for hydrocarbon flames generally, because it has been proved experimentally that acetylene is not necessarily either a prime or principal product of the thermal decompositions of hydrocarbons; indeed, in most cases, it is only produced in quite unimportant proportions, and sometimes even not at all.

Before, however, considering the modes in which the simpler hydrocarbons decompose at high temperatures, attention may be drawn to certain facts which have been established concerning the behaviour of some of the paraffins higher than methane and ethane. In 1873 T. E. Thorpe and J. Young,* as the result of an investigation of the combined action of heat and pressure on the paraffins, concluded that their primary decomposition gives rise to an olefine and a lower paraffin without loss of hydrogen, somewhat as follows :

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 = CH_3 \cdot CH_3 + CH_2 : CH_2.$$

Moreover, in 1886, H. E. Armstrong and A. K. Miller,† during an exhaustive investigation of the products obtained in the manufacture of 'oil gas' from petroleum, found considerable quantities of ethylene and normal olefines of the type $(C_nH_{2n+1})CH : CH_2$, up to and including *n*-heptylene, as well as of benzonoid hydrocarbons. They also called particular attention to the almost entire absence of acetylene or its homologues, and suggested the possibility of the direct formation of aromatic hydrocarbons from the corresponding paraffins (say benzene from hexane) without the interaction of acetylene.

Finally, in 1896, F. Haber ‡ published a paper on the decomposition of the higher hydrocarbons, in which he vigorously assailed the theories of both Berthelot and Lewes, and proved conclusively that in the case of *n*-hexane, which was selected as being the paraffin most nearly related to benzene, the primary decomposition at temperatures between 600° and 800° C. involves the elimination of methane and the formation of the next lower olefine, (amylene), without any appearance of acetylene whatsoever, a behaviour which he regarded as typical of all the higher paraffins, thus :

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* *Proc. Roy. Soc.* 21, p. 184.

† *Journ. Chem. Soc.* 49, p. 74.

‡ *Ber.* 29, p. 2191.

$$CH_3 \cdot (CH_2)_n \cdot CH_2 \cdot CH_2 \cdot CH_3 = CH_3 \cdot (CH_2)_n \cdot CH : CH_2 + CH_4.$$

In the aromatic series, however, he recognised a marked disposition to form more complex molecules with the elimination of hydrogen, *e.g.* diphenyl from benzene.

It is interesting to note, in passing, that whilst Haber thus rejected *in toto* the Berthelot-Lewes theories as untenable, he nevertheless accepted the then prevailing notion, which subsequent research has disproved, of the inherent superior stability of acetylene over that of all other hydrocarbons at high temperatures. For he stated that, whilst it polymerises readily at 600°, and at 800° yields large quantities of hydrogen, it is at still higher temperatures "*in starker Verdünnung jedem anderen Kohlenwasserstoff an Beständigkeit überlegen.*"

The researches of W. A. Bone and H. F. Coward upon the behaviour of the simpler hydrocarbons, methane, ethane, ethylene and acetylene at temperatures between 500° and 1200° C. have shewn that these decompositions are far too complex to be represented by ordinary chemical equations. For details of their experiments the original paper must be consulted *; here we need only deal with the general character of the results, and the conclusions drawn from them.

Experiments upon methane shewed, not only that it is by far the most stable of all hydrocarbons at the temperature of ordinary flames, but also that it is always a principal product of the decomposition of the other three, especially at temperatures above 800° C. Moreover, unlike that of the other hydrocarbons, its decomposition up to 1200°, and probably far beyond, is entirely a 'surface' effect, involving the direct formation of hydrogen and carbon, the latter being deposited on the walls of the reaction tube in a peculiarly hard and lustrous form ('methane-carbon') quite different from the dull soft variety yielded by acetylene under similar conditions. The normal decomposition is really a reversible change,

$$CH_4 \rightleftharpoons C + 2H_2,$$

because, as Bone in conjunction with Jerdan and Coward has shewn,† it can be synthesised from its elements both at 1000°–1200° and at the temperature of the electric arc. Apparently, acetylene is not so formed until a temperature of about 1800° C. is reached.

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* *Trans. Chem. Soc.* 93 (1908), p. 1975; 97 (1910), p. 1219.

† *Trans. Chem. Soc.* 71 (1897), p. 41; 79 (1901), p. 1042; 93 (1908), p. 1975; and 97 (1910), p. 1219.

In 1919 H. F. Coward and S. P. Wilson determined the composition of the equilibrium mixture of methane and hydrogen in contact with amorphous carbon at atmospheric pressure to be as follows :*

Temperature °C.	850°.	1000°.	1100°.
CH_4	2·5	1·1	0·6
H_2	97·5	98·9	99·4

Concurrently with its principal decomposition, it was observed by Bone and Coward that, when undiluted methane is introduced into a vacuous tube between 1000° and 1200°, a short period ensues during which highly condensed layers of the gas are decomposing in contact with the walls, and that, during such abnormal conditions, minute quantities of acetylene and even benzene are, or may be, formed. Such conditions hardly pertain to ordinary flames, although it seems possible that they might do so in combustion at high pressures. Methane is strongly exothermic, its molecular heat of formation being +21·7 calories; and, having regard to its relatively great stability at ordinary flame temperatures, the feeble luminosity of its flame is quite understandable. Indeed methane has been found to be surprisingly stable, and difficult to resolve into its elements, even during the drastic conditions of explosions at high pressures. There never was any clear evidence supporting the Berthelot-Lewes view of its thermal decomposition being primarily into acetylene and hydrogen, thus :

$$2CH_4 = C_2H_2 + 3H_2.$$

Moreover, if such were the case, and Lewes' acetylene theory of luminosity correct, there seems no reason why a methane flame should be so feebly luminous as it is at ordinary pressure. On the contrary, we should expect it to be highly luminous, although from what was said in the previous paragraph it would not be surprising if it were to develop greater luminosity when burning at high pressure, which would be an interesting experiment to try.

The thermal decompositions of the other three hydrocarbons examined (ethane, ethylene and acetylene) were found to be no longer mere 'surface' effects, but to take place homogenously throughout their bulk. All of them yield a cloud of carbon particles (lamp black) at temperatures of 800° C. and upwards. The conclusions drawn by Bone and Coward from their experiments concerning the essential features of the phenomena were that in the cases of ethane and ethylene the primary effect of heat is to cause an elimination of hydrogen, together with a simultaneous loosening or dissolution (according to temperature) of the bond between the carbon atoms, giving rise (in the event of dissolution) to residues such as $:CH_2$ and $\vdots CH$. These residues, which can only have a very fugitive separate existence, may subsequently *either* (*a*) form $H_2C:CH_2$ or $HC \vdots CH$, as the result of encounters with other similar residues, *or* (*b*) break down directly into carbon and hydrogen, *or* (*c*) be directly hydrogenised to methane in an atmosphere of hydrogen. All these possibilities may be realised simultaneously in the decomposing gaseous medium in proportions dependent upon the pressure, temperature, and amount of hydrogen present. Moreover, (*d*) 'condensations' of nascent molecules such as $H_2C:CH_2$ or $HC:CH$, in process of formation during the primary dehydrogenation, are also possible, especially when they are present in great concentration, so that aromatic nuclei might conceivably arise immediately after the primary dehydrogenation. The scheme for ethane and ethylene may be represented as follows:

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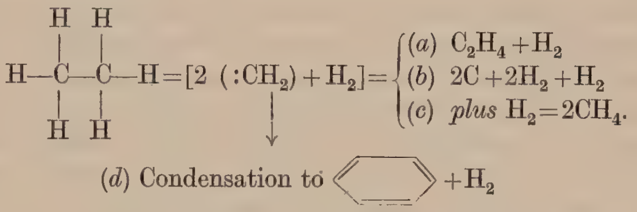
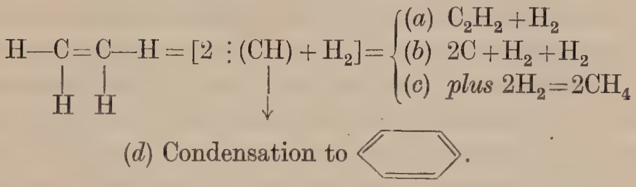
* *Trans. Chem. Soc.* 115 (1919), p. 1380.

(1) 

$$H_3C{-}CH_3 = [2\,(:CH_2) + H_2] = \begin{cases} (a)\ C_2H_4 + H_2 \\ (b)\ 2C + 2H_2 + H_2 \\ (c)\ \textit{plus}\ H_2 = 2CH_4. \end{cases}$$

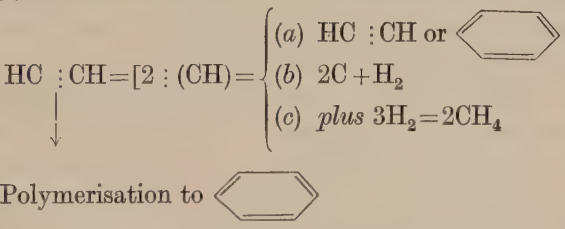
(*d*) Condensation to $+H_2$

(2) 

$$H{-}CH{=}CH{-}H = [2\,:(CH) + H_2] = \begin{cases} (a)\ C_2H_2 + H_2 \\ (b)\ 2C + H_2 + H_2 \\ (c)\ \textit{plus}\ 2H_2 = 2CH_4 \end{cases}$$

(*d*) Condensation to .

In the case of acetylene, the main primary change seemed to be one of polymerisation or of dissolution, according to the temperature; in the latter event, it may be supposed that residues $:CH$ are first formed, and subsequently either (*a*) recombine with others, (*b*) break down into carbon and hydrogen, or (*c*) are hydrogenised to methane, according to circumstances, as follows:

(3) 

$$HC\,:CH = [2\,:(CH) = \begin{cases} (a)\ HC\,:CH\ \text{or} \\ (b)\ 2C + H_2 \\ (c)\ \textit{plus}\ 3H_2 = 2CH_4 \end{cases}$$

(*d*) Polymerisation to

With regard to the possible secondary changes (*a*), (*b*) and (*c*) in such systems, it may be supposed that, in general, the proportion of (*b*) would increase with the temperature, whilst that of (*a*) would be influenced in the opposite sense. The occurrence of (*c*), which would obviously depend on the amount of hydrogen in the system at any given moment, is doubtless favoured by a temperature range of 800° to 1000°. Condensations or polymerisations (*d*) in the system are essentially what may be termed 'low medium' temperature effects, a range of 500° to 700° being certainly a favourable one, as experiments with acetylene have proved. Moreover, at temperatures above 800°, the secondary slow decomposition of any methane produced by the 'hydrogenations' (*c*) must be reckoned with as an after-effect the importance of which increases with the temperature.

So much attention having been directed in the past to the behaviour of acetylene, perhaps the following additional point may be noted. The susceptibility of the gas to polymerise is easily demonstrated at temperatures between 500° and 700°, especially at the latter. Above 700° the tendency to polymerise rapidly diminishes, while the direct resolution into carbon and hydrogen increases, until at 800° the undiluted gas undergoes the characteristic instantaneous luminous decomposition first observed and described by V. B. Lewes. Indeed, in one experiment made by Bone and Coward, about 75 per cent. of the gas was decomposed at 800° during the first 'flash,' the remaining 25 per cent. afterwards underwent quiet decomposition during a period of over fifteen minutes under conditions which strongly favoured the hydrogenation of the $:CH$ residues to methane.

The behaviour of undiluted ethylene within the range of 500° to 700° is very interesting. Bone and Coward found that the $:CH$ residues, formed by the primary decomposition at first rapidly coalesced forming acetylene, but as hydrogen accumulated in the system the tendency for them to be hydrogenised to methane became progressively more marked. Aromatic hydrocarbons were continuously produced, either by the secondary polymerisation of acetylene, or by the coalescence of $:CH$ residues. Only a very small proportion of the carbon in the gas was liberated in the free state (thus at 570° only 0·75 per cent. of it). At 800° the tendency to form aromatic hydrocarbons was very much less, and the separation of carbon larger, than at the lower range. The predominant effect was the hydrogenation of the $:CH$ residues to methane. So marked was the last-named tendency that methane was found to constitute as much as 67·7 per cent. of the final gaseous products at 800° just when the last remains of the original ethylene were disappearing. At 1000° not more than about 4 per cent. of the original gas was converted into condensable aromatic hydrocarbons during the initial rapid decomposition. The hydrogenation of $:CH$ residues to methane was still a dominant feature of the phenomena, although the tendency of free carbon to be liberated increased.

In the case of ethane, experiments at 675° C. shewed primarily a strong tendency for the coalescence of $:CH_2$ residues forming ethylene, which latter in a diluted condition decomposed, *via* $:CH$ residues, yielding eventually a mixture of carbon, hydrogen and methane, with some intermediate formation of acetylene. There was only a very small yield of aromatic hydrocarbons (equivalent to not more than 4 per cent. of the original gas) nearly all in the form of almost pure naphthalene (no benzene). Thus the behaviour of ethane at such low temperatures was in strong contrast to that of either ethylene or acetylene in respect of ‘ aromatic ’ formations. At 800°, whilst the primary $:CH_2$ residues still shewed a marked tendency to coalesce to ethylene, their hydrogenation to methane now became the predominant feature, and remained so until after a temperature of 1000° had been passed. The amount of ‘ aromatics ’ formed during a brief heating to the latter temperature was again only about 4 per cent. of the total ethane changed. It is conceivable that $\cdot CH_3$, as well as $:CH_2$, residues might be primarily formed, in which case they would probably undergo either (*a*) dissolution into carbon and hydrogen, or (*b*) hydrogenation to methane, according to circumstances.

Whilst most authorities will probably agree that the separation of finely divided carbon in the thermal decompositions of such hydrocarbons is in all probability a potential cause of the luminosity of their flames, it needs to be emphasised that, with the possible exception of acetylene, their rates of decomposition are far slower than those of their combustion at the temperatures prevailing in flames. This fact, coupled with their undoubted great affinities for oxygen, impels us to the conclusion that in the propagation of a flame through a homogeneous mixture of a hydrocarbon and oxygen (air), oxidation will probably take precedence of all other chemical phenomena. Hence in such cases we must also look to the thermal decompositions of hydroxylated molecules and aldehydes (but not formaldehyde) as at least a contributory, if not the main, cause of ‘ carbon deposition,’ as indicated in the previous chapter.

The strongly endothermic character of acetylene, coupled with its explosive ‘ flash ’ decomposition at the temperatures prevailing in flames, would probably also constitute it a contributory factor in special cases, *e.g.* in acetylene and possibly also ethylene flames, although not in hydrocarbon flames generally.

CHAPTER XXXIII

THE COMBUSTION OF CARBON DISULPHIDE

THE combustion of carbon disulphide (b.p. 46·2° C.) presents so many features of interest to chemists that a separate chapter may be devoted to their consideration.

As long ago as 1813 Berzelius and Marcet exploded in a eudiometer a mixture of oxygen with excess of carbon disulphide, and, after removing sulphur dioxide and carbon dioxide from the products, they obtained a residue containing carbon monoxide. They also noticed that some drops of liquid had condensed on the side of the tube.*

Fifty years later E. Frankland found the ignition point of the vapour in air to be 300° F. (149° C.),† but he does not seem to have investigated the chemical aspects of its combustion.

Favre and Silbermann were the first to determine (1852) its molecular heat of combustion, which they found to be 258·5 K.C.U.S; this being greater than the sum of the heats of combustion of its constituent elements $(97+2\times72=241)$ the endothermic character of the substance was established. Subsequently, Julius Thomsen found the molecular heat of combustion to be 265·1 for the liquid and 258·7 K.C.U.S for the vapour when burnt at constant pressure. Berthelot found 253·3 K.C.U.S for the vapour at constant pressure. According to Thomsen the molecular heat of formation of the vapour is −28·7 K.C.U.S and of the liquid −22·3 K.C.U.S.

In 1888 H. B. Baker ‡ shewed that a mixture of carefully purified and dried carbon disulphide and dried oxygen exploded apparently at the same temperature, and with as much violence, as when moisture was present. This result he remarked "was the more surprising, as the elements of which the bisulphide is composed do not burn in oxygen, even when very strongly heated," referring, of course, to *dry* systems. He thought, however, that it might be due to the bisulphide having been decomposed by the shock of the explosion, and he proceeded to shew that whereas a temperature of 258° to 260° C. is required for explosion of the *dried* $CS_2 + O_2$ mixture used, the CS_2-vapour begins to decompose at 201° when heated by itself.

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* *Phil. Trans.* 1813, p. 171.

† *Chemical News*, 6 (1862), p. 3.

‡ *Phil. Trans.* 179 (1888), p. 582.

In 1890 Pedler exploded mixtures of carbon disulphide with air and oxygen and shewed that, owing to the great amount of heat evolved, some of the nitrogen was oxidised.*

In the same year G. S. Turpin † discovered that a stream of air or oxygen after passage over liquid carbon disulphide could be made to 'glow' in a glass tube heated to 200° without bursting into flame, depositing a reddish-brown volatile solid on the glass with simultaneous formation of sulphur dioxide. This phenomenon is sometimes referred to as the 'phosphorescent combustion' of carbon disulphide. He also observed the following ignition temperatures :

Mixture.	Ignition Temperature °C.
$CS_2 + 10O_2$	160°
$CS_2 + 5O_2 + 5N_2$	175°
$CS_2 + 5O_2 + 5CO_2$	175°
$CS_2 + 5O_2 + 5SO_2$	260°

It is, however, to H. B. Dixon and his collaborators that we owe most of our knowledge concerning the matter, and we will now summarise the more important results of their investigations.

In the first place, by means of his new concentric tube apparatus (see Chapter VIII, Fig. 6), Dixon determined the ignition points of carbon disulphide alone, as well as in admixture with equal volume of other gases, when heated in air or oxygen, with the following interesting results : ‡

TABLE CXII.—IGNITION-POINTS OF CARBON DISULPHIDE ALONE AND MIXED WITH EQUAL VOLUMES OF OTHER GASES (DIXON)

Lag. (secs.).	CS_2.		$CS_2 + N_2$.		$CS_2 + CO_2$.		$CS_2 + H_2$.	
	Oxygen.	Air.	Oxygen.	Air.	Oxygen.	Air.	Oxygen.	Air.
0·5	132°	156°	140°	161°	144°	163°	161°	171°
1	128	151	134	155	139	157	157	167
2	123	145	126	147	132	148	149	161
3	118	138	120	139	125	139	140	153
5	114	130	116	132	120	132	131	145
7	110	124	112	127	116	127	122	138
10	107	120	109	122	113	122	116	134

These results, he remarked, " brought out clearly the power of carbon disulphide when mixed with other gases to maintain the ignition point of the mixture at a low temperature—approximating to its own."

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* *Trans. Chem. Soc.* 57 (1890), p. 625.

† *Brit. Assoc. Reports*, 1890, p. 776.

‡ *Rec. des. Trav. Chim. des Pays.-Bas*, 46 (1925), pp. 305-322.

In regard to the probable connection between the phosphorescent combustion of carbon disulphide and its low ignition temperature, Dixon has shewn that whereas some gases, such as hydrogen, carbon dioxide and nitrogen, merely act as diluents, and others, such as sulphur dioxide, carbon monoxide, methane, etc., merely enfeeble, but do not extinguish, the phosphorescent flame when added to the vapour in small quantities, ethylene and acetylene both extinguish it, and raise the ignition temperature, even when present in small quantities only. In illustration of this point we may reproduce his determinations of the ignition temperatures of equimolecular mixtures of carbon disulphide with methane, ethylene, or acetylene, respectively, as follows:

TABLE CXIII.—IGNITION TEMPERATURES OF EQUIMOLECULAR MIXTURES OF CARBON DISULPHIDE WITH METHANE, ETHYLENE OR ACETYLENE (DIXON)

Mixture.	$50 CH_4 + 50 CS_2$.		$50 C_2H_4 + 50 CS_2$.		$50 C_2H_2 + 50 CS_2$.	
	In O_2.	In Air.	In O_2.	In Air.	In O_2.	In Air.
Lag. (secs.).	°C.	°C.	°C.	°C.	°C.	°C.
0·5	173	195	535	608	434	520
1	164	185	524	596	421	514
2	154	174	512	571	400	500
3	145	162	505	555	378	485
5	137	149	496	541	356	470
7	132	138	487	535	338	455
10	—	134	482	528	322	442
15	—	—	475	522	310	430

Indeed, so powerful was the inhibiting effect of ethylene upon the phosphorescent combustion of carbon disulphide that the addition of only 0·5 per cent. of it to a $95H_2 + 5CS_2$ mixture, whose ignition temperature in air after 0·5 second lag was 215° C., raised it to 405° C.

Dixon's conclusion was that the 'phosphorescent flame' of carbon disulphide is conditioned by the formation of the reddish-brown volatile solid deposit observed by Turpin, and which is probably carbon monosulphide. On such supposition the main reaction involved may be represented by the equation:

$$CS_2 + O_2 = CS + SO_2.$$

He observed that this "brown red film of carbon monosulphide deposited on the heated walls can itself become luminous and start the phosphorescent flame," also that a trace of any gas which 'poisons' the phosphorescence also inhibits the formation of the deposit. The ethylene or other ‘poison-gas’ has no inhibiting effect when introduced into the phosphorescent flame itself; to be effective it must be mixed either with the unburnt carbon disulphide vapour, or with the air, *before they begin to react.*

He also shewed that the phosphorescent flame readily passes through a metallic gauze which cuts off an ordinary flame, thus confirming Davy's prediction that such a cool flame would pass through a gauze.

The whole matter is of great interest in that it suggests that an inflammable gas may possibly *begin* burning by a similar process of phosphorescent combustion, and shews what important results might accrue from a systematic study of such low temperature ‘phosphorescent’ flames.

In 1899 Dixon and E. J. Russell published the results of a very complete study of the combustion of carbon disulphide under a variety of conditions.* Their principal observations and conclusions were as follows:

(1) H. B. Baker's conclusion that *dryness* does not affect its burning was confirmed.

(2) With regard to the ‘phosphorescent combustion,’ it was shewn that when a stream of air and oxygen is passed first over carbon disulphide, and then through a glass tube heated to 200° C., the ‘glow’ can be maintained for any length of time; sulphur dioxide is formed, and a reddish-brown volatile substance (‘carbon subsulphide’) condenses.

(3) Carbon disulphide was found to be comparatively stable when heated; at 230° prolonged heating was necessary before the slightest decomposition could be noticed, and no change was observed on passing the vapour through a tube kept at 400° C. Consequently it seemed unlikely that the combustion of carbon disulphide is preceeded by a decomposition into its elements.

(4) The reaction occurring when carbon disulphide is exploded with oxygen cannot be expressed by any simple equation—because:

(*a*) when excess of oxygen is used, the products are carbon dioxide, sulphur dioxide, sulphur trioxide, and sometimes free sulphur; in the explosion wave, carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide result.

(*b*) with defect of oxygen, the products are carbon dioxide, sulphur dioxide, carbon monoxide, carbonyl sulphide, and carbon disulphide; as the proportion of oxygen present in the explosive mixture is progressively diminished the proportion of sulphur dioxide produced falls off, whilst those of the other products increase.

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* *Trans. Chem. Soc.* 75 (1899), pp. 600-613.

(c) even with small amounts of oxygen there is always a division of it between the carbon and sulphur; *e.g.* using a mixture $CS_2 + \frac{1}{2}O_2$ only a portion of the CS_2 takes part in the reaction.

(5) The following analyses were given of the gaseous products obtained when various mixtures with defect of oxygen were exploded:

TABLE CXIV.—GASEOUS PRODUCTS FROM THE EXPLOSION OF CARBON DISULPHIDE WITH DEFECT OF OXYGEN (DIXON AND RUSSELL)

Original Mixture.	Percentage Composition of Gaseous Products.			
	SO_2.	CO_2.	CO.	$COS + CS_2$.
$CS_2 + 2O_2$	51·4	37·6	6·2	2·7
$CS_2 + 1\frac{1}{2}O_2$	39·9	38·7	12·9	5·2
$CS_2 + O_2$	25·4	38·7	26·1	6·2
$CS_2 + 0{\cdot}55O_2$	4·4	21·0	56·0	19·8

(6) The following 'rates of explosion' for CS_2-oxygen mixtures were determined:

Mixtures.	Metres per Sec.
$CS_2 + O_2$	1592
$CS_2 + 1\frac{1}{2}O_2$	1702
$CS_2 + 2O_2$	1751
$CS_2 + 3O_2$	1802
$CS_2 + 4O_2$	1753
$CS_2 + 5O_2$	1732
$CS_2 + 6O_2$	1640

It should be noted that the *maximum* velocity observed was for the 'theoretical mixture' $CS_2 + 3O_2$, a circumstance which may be contrasted with all the cases of hydrocarbons hitherto examined (*vide* Chapter XVI, p. 179). The 'richest' mixture which could be made to 'detonate' by any of the methods used contained $1\frac{1}{2}$ volumes of CS_2 to 1 volume of oxygen; and so poor a mixture as 1 volume of CS_2 to 7 volumes of oxygen would still detonate.

(7) When burnt in a Smithells' flame-separator the outer cone was pale blue, shewing a bright continuous spectrum. On introducing a cold porcelain surface into it a deposit of sulphur was obtained, but no carbon separated. Sulphur was also deposited in the space between the two cones. The inner cone was greenish-grey in colour, and also gave a bright continuous spectrum. The interconal gases contained 10·3 to 11·3 per cent. of SO_2, 9·5 to 11·7 per cent. of CO, 0·75 to 2·5 per cent. of $CO_2 + COS + CS_2$, and 74·5 to 78·2 per cent. of N_2. In other words, the products from the inner cone consisted mainly of equal volumes of carbon monoxide and sulphur dioxide.

(8) The combustion of carbon disulphide differs from that of all other carbon compounds hitherto investigated in that (*a*) carbon is not deposited, (*b*) the explosion wave is not propagated through a $2CS_2 + O_2$ mixture, and that the equation $2CS_2 + O_2 = 2CO + 2S_2$, analogous to

$$C_2H_4 + O_2 = 2CO + 2H_2$$

could not be realised, and (*c*) the maximum velocity of detonation is attained with the 'theoretical' $CS_2 + 3O_2$ mixture, containing sufficient oxygen to burn the carbon to carbon dioxide and the sulphur to its dioxide.

Quite recently, A. G. White, of Nobel's Research Department, who had previously found the limits of downward self-propagation of flame in carbon disulphide-air mixtures at atmospheric temperature and pressure to be between 1·9 and 35·0 per cent. of the combustible, has published a further paper * in which he says that, *when burning alone,* any CS_2-air mixture can propagate flame if its calorific value exceeds 530 cals., but that what may be termed the 'lower limit' of combustion is specifically catalysed, probably by some product of its partial combustion such as the monosulphide or the oxysulphide. This effect is hindered by the pressure of one or other of a large variety of other combustible substances, where efficacy is in the following diminishing order, namely, pentane and ethyl ether, ethylene, ethyl alcohol, acetylene, benzene, acetone, hydrogen sulphide, acetic acid, methane, hydrogen, cyanogen, and carbon monoxide. Further research, however, is needed before a satisfactory explanation of such results can be reached.

* *Trans. Chem. Soc.* (1927), pp. 793-802.

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SECTION V

CHAPTERS XXXIV TO XXXVI

CATALYTIC AND INCANDESCENT SURFACE COMBUSTION

CHAPTER XXXIV

THE REVIVAL OF CATALYTIC COMBUSTION

Introduction

It has been related in Chapter V. that many important investigations were made by leading chemists during the period 1819 to 1835 upon the phenomenon of catalytic combustion which Davy had discovered in 1817. After the controversy between Faraday and de la Rive in 1834-5 all interest in the matter seems suddenly to have evaporated, and hardly anything of importance was heard about it during the next half century.

Meanwhile, the researches of Deville upon the dissociation of steam and carbon dioxide at high temperatures, in which he had employed incandescent surfaces, had begotten the wholly erroneous notion that because such surfaces promote dissociation they must necessarily hinder combustion. Frederick Siemans strongly upheld this view, and so great was his influence upon contemporary thought respecting gaseous combustion that his dictum was accepted without question for a generation.

Siemans was of the opinion that inasmuch as "a flame consists of a chemically excited mixture of gases whose particles are in violent motion . . . it follows that any solid substance brought into contact with gases thus agitated must necessarily have an impeding effect upon their motion . . .; in the immediate neighbourhood of such surfaces the combustion of gases will cease altogether, because the attractive influence of the surfaces will entirely prevent their motion." * Moreover, in regard to dissociation, he pointed out that Deville and others had used in their experiments small vessels of special material, which (as he thought) by some peculiar influence upon the surrounding gaseous medium had directly caused the dissociations observed by them. Hence he concluded "that solid surfaces have a twofold influence upon combustion. In the first place they hinder combustion because they interfere with the rapid motion of the gases necessary for combustion; and in the second place they cause dissociation . . ." In furnace operations, "neither the employment of gases in proper proportion, nor their proper mixture is sufficient to ensure perfect combustion if the disturbing influence of surfaces is allowed to interfere to prevent combination, or to dissociate particles of gas already combined . . . surfaces not only interfere with combustion . . . but also . . . if heated, they facilitate dissociation ; that, in fact, dissociation, which has hitherto been thought to be brought about by the influence of heat alone, was in reality caused by the action of heated surfaces upon the combined gases ; or, at all events, that in the absence of surfaces the temperature of dissociation would be very much higher." Hence, "complete combustion is impossible whenever the live or active flame is allowed to come in contact with any solid surfaces." *

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* *Proc. Roy. Institution*, xi. (1884-6), p. 471.

It is perhaps hardly necessary to point out, that, whilst it is true that a *cold* surface thrust into a flame will cool below the ignition point the layer of combining gases in its immediate vicinity and so prevent completion of combustion, an incandescent surface undoubtedly accelerates combustion. Indeed, the fact that an incandescent surface accelerates dissociation necessarily implies that it will also accelerate the combination of the products thereof.

Thomas Fletcher of Warrington, who did so much forty years ago to develop the uses of gas in small scale heating operations, seems to have had a clearer conception than any of his contemporaries concerning the influence of hot surfaces in combustion. For, in a lecture at the Manchester Technical School in 1887, entitled "Some Curious Flames," he demonstrated the possibility of realising a flameless surface combustion in contact with metals other than those of the platinum group. He said, "I will now dispense with flame altogether, and show you the same quantity of gas and air burning as before, but in the most perfect form, the combination taking place on the surface of the substance to be heated without any flame. To show this so that all can see, the mixture of gas and air is directed on to a large ball of iron wire, flame being used at first to heat the wire to the temperature necessary to continue the combustion. By stopping the gas supply for an instant the flame is extinguished, and the combustion is now continued without any flame, but with an enormous increase in the heat obtained. This invisible or flameless combustion is only possible under certain conditions ; and one essential point is that the combustible mixture shall come into absolute contact with a substance at a high temperature which is capable of absorbing the heat as it is generated. . . . In the absence of a solid substance at a high temperature, it is impossible to cause combustion without flame ; and when a flame is used it is also impossible to make it touch a cold surface."

It has been said sometimes that Fletcher never got beyond Davy's conception of surface combustion ; but a moment's reflection will shew that in one important particular, he did. For Davy never really got so far as to conceive of an *intensification* of ordinary flame combustion by a glowing surface of platinum; indeed, his only idea seems to have been that, "inasmuch as the temperatures of flames far exceed those at which solids became incandescent, a metallic wire can be maintained in a state of glow by the flameless combustion of gases at its surface." Fletcher, on the other hand, thought that the change over from the ordinary flame to the flameless combustion of gases and air in contact with his iron ball resulted in "an enormous increase in the heat obtained," by which he obviously meant a higher temperature. Unfortunately, however, he did not follow up the matter, and his exposition of it had little influence upon contemporary thought.

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* *Jour. Iron and Steel Inst.* 1886, ii. pp. 685-693.

A great many circumstances during the 'nineties,' however, directed the attention of chemists once again to the problem of the influence of hot surfaces upon combustion and other gaseous interactions. In this connection it need only be recalled how the efforts of Victor Meyer and others to determine accurately the ignition temperatures of explosive mixtures (*vide* Chapter VIII), were largely thwarted by irregularities which could only be attributed to the influence of the hot walls of the containing vessels; and experiments by other workers upon the velocities of chemical interactions in gaseous systems gave results which were difficult to understand except on the supposition of the intervention of some accelerating surface action.

Some General Considerations

It is now generally recognised by chemists that in principle all hot surfaces have an accelerating influence upon chemical change in gaseous systems; or, in other words, that if at any temperature a gaseous system A tends to pass over into another system B, contact with a solid at that temperature will accelerate the process.

It is therefore necessary to distinguish between two possible conditions under which gaseous combustion may occur, namely, (1) *Homogeneously*—that is to say, equally throughout the system as a whole, at temperatures *below* the ignition point *slowly* and *without flame*, and at temperatures *above* the ignition point *rapidly* and *with flame*; and (2) *heterogeneously*, or, only in layers immediately in contact with a hot or incandescent surface ('surface combustion'). It is also necessary to remember that, *ceteris paribus*, the heterogeneous incandescent surface combustion is a faster process than the normal homogeneous combustion of ordinary flames.

Catalytic combustion is, however, so complex a phenomenon, and its experimental investigation so full of pitfalls for the unwary, that we are still much in the dark as to its true cause. Possibly even several factors may operate simultaneously in any given case, and much further patient research will be needed before everything is understood.

There is, however, much evidence indicating that in catalytic combustion the combining gases (or at least one of them) undergo an ‘ activation ’ of some sort by association with the surface prior to being burnt. If this be so, then in an irreversible heterogeneous reaction of the type $A+B=AB$, presumably we have to consider such factors as (i) the rates at which A and B respectively diffuse inwards from the surrounding atmosphere on to the surface, (ii) the rates at which A and B (or one of them) are ‘ activated ’ at the surface, (iii) the rate at which the ‘ activated ’ gases combine, and (iv) the rate at which the product AB ‘ evaporates ’ or diffuses away from the surface. Presumably also all such rates will vary differently with temperature and pressure, and the rate of formation of AB actually observed in any given circumstances will be controlled by the *slowest* of them.

We can, therefore, conceive the possibilities of several extreme or limiting cases. For example, (1) if in any particular case (iii) were infinitely great as compared with all other factors, and (ii) greater than either (i) or (iv), then the observed rate of reaction would be governed by diffusion factors. Such a condition would be indicated if and when—with the reactants present in other than their combining ratios—the observed rate of combination is governed by the concentration of the one in defect. Or again, (2) if (ii) were much less than either (i) or (iii), and (i) be greater than (iii), the observed rate would be governed by the rates at which the reactants (or one of them) are ‘ activated ’ at the surface. Similar considerations would apply in other conceivable circumstances, so that each particular case should be carefully studied with all such possibilities in mind.

Another factor which must be considered also is the condition of the surface itself. Thus, for example, in given circumstances a metal surface may be capable of changing slowly from an amorphous to a cystalline state (or *vice versa*), or from one cystalline state to another. Surfaces composed of easily reducible oxides or oxidisable metals obviously may undergo considerable change; indeed, according to one school of thought, catalytic combustion is essentially a rapidly alternating oxidation and reduction of the surface. A metal surface when freshly reduced may be a more potent catalyst than later on, and similarly with a freshly oxidised surface.

In this connection, also, must be considered the possibility of the surface being more or less ‘ lagged ’ by either inert gases (nitrogen or steam) or by the products of combustion. The catalysing power of a surface towards a combining system $A+B=AB$ in any given circumstances must always depend upon the proportion of its total area actually exposed to the reactants. Now it is well known that at all temperatures surfaces attract and retain ‘ condensed ’ layers of gases, and this applies both to inert gases and to products of combustion as well as to reactants. Whatever portion of the surface may be so ‘ lagged ’ by nitrogen, steam, or carbon dioxide at any given instant is definitely ‘ out of action ’ so far as the reactants are concerned. Thus, for example, it has recently been shewn that the hygroscopic state of a reacting system may be an important factor in regard to the rate of combination, owing to such ‘ lagging ’ of the surface by steam ; and much evidence can be adduced that nitrogen also is capable of ‘ lagging ’ a surface.

It is important also to distinguish between the parts played by merely *adsorbed* gas-films and deeply *occluded* gases, respectively, because recently there has been a tendency in some quarters to overlook the latter, and to ascribe everything to the former. This aspect of the matter is bound up with what is implied by the word ‘ surface ’ in such connection. Ordinarily it would imply what can be recognised by the eye as the bounding surface of a solid ; but, inasmuch as we know that all solids are merely lattices of atoms separated by empty spaces, scientifically the expression ‘ surface ’ implies much more. For, whilst presumably the outermost atoms of such a lattice will have a greater power than those inside it of influencing the stability of such gaseous molecules as may be within range at any instant, we have no right to assume that it is only the outermost atoms that can be effective. And if, for example, it should eventually be proved that catalytic combustion depends upon a primary ‘ ionisation ’ of the reactants (or one of them), the influence of the *inner* atoms of the lattice upon ‘ occluded ’ (as distinct from merely ‘ adsorbed ’) gases could hardly be dismissed as unimportant.

In investigating the subject experimentally, up to now the usual practice has been to select a simple case such as that of hydrogen and oxygen in contact with some convenient surface at a temperature where the reaction velocity is both measurable and well under control, and to study how it varies with the partial pressure of each of the reactants, respectively, as well as with other ascertainable circumstances. And, unless very low gas pressures are used, such investigations necessarily have to be conducted not only at comparatively low temperatures, but also within limits of temperature separated at most by two or three hundred degrees. Attempts have been made to carry out such experiments at fairly high temperatures, but usually in such circumstances only very low gas pressures can be employed. Hence the range of conditions over which such velocity measurements can be made is necessarily circumscribed ; therefore, in such wise we can only make a partial study of the phenomena, and ought to recognise the limitations of our methods.

It is necessary also, in any given circumstance, always to ensure (i) that we are dealing with a catalytic combustion only, (ii) that the surface itself is not changing during the process in an unknown and uncontrolled manner , (iii) that the hygroscopic condition of the system is accurately known, also whether or not the presence of steam (apart from its possible 'lagging' effects) is essential to its working, and (iv) that the reaction product is quickly removed from the system.

Another consideration which needs stressing is the danger of basing general theories upon the results of experiments with one or two surfaces only, or with insufficient variations in conditions. When such theories are advanced, it behoves us to scrutinise most carefully the experimental evidence supporting them, and to accept only such as appear conclusive; for in few branches of experimental work is there greater need for a severely critical attitude.

Bodenstein's Researches

M. Bodenstein was almost the first to attempt the experimental measurement of reaction velocities in cases of catalytic combustion, and the complexity of the phenomena was soon apparent from his work.

In 1899 he published some experiments upon the non-explosive combination of electrolytic gas during its passage through a glazed porcelain tube or vessel maintained in a lead bath at various constant temperatures between 482 and 689° C.* There were admittedly two inherent sources of error in this method, namely (i) that it was impossible to maintain a sharp limit between the heated and unheated portions of the reaction vessel and its connections, and (ii) the reacting mixture was not instantly raised to the temperature of the bath. These, however, were reduced to a minimum by having the volume of the heated relative to the unheated part of the vessel relatively large. Notwithstanding such precaution, however, he suspected there was some source of error influencing the results irregularly '*in oft recht unliebsamer Weise*,' so that it seems difficult to gauge their significance. The surface/volume (s/v) ratios of the reaction vessels employed were 1·63, 4·77 and 14·0 respectively. From the fact that the rate of combination observed at any particular temperature increased with the surface/volume ratio of the reaction vessel, he concluded that he was dealing with a catalytic combustion entirely; but his results, which he regarded as satisfying broadly the equation for a reaction of the third order, pointed to the actual rate of combination at the surface having been very much smaller than any of the other factors concerned.

Of his experimental results for undiluted electrolytic gas, the following may be quoted in this connection, the k values being the velocity constants calculated from the 'third order' equation.

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* *Zeit. physik. Chem.* 29 (1899), pp. 665-699.

TABLE CXV.—BODENSTEIN'S EXPERIMENTS WITH ELECTROLYTIC GAS IN CONTACT WITH A GLAZED PORCELAIN SURFACE

	Tube I. s/v=1·63.	Tube III. s/v=14·0.
Temperature C°.	k Values.	k Values.
482°	0·053 to 0·0829	0·244 to 0·339
509°	0·184 to 0·398	1·06 to 1·48
560°	0·96 to 2·44	4·26 to 9·78

In 1903 Bodenstein published an illuminating paper embodying the results of experiments on the combination of hydrogen and oxygen in contact with platinum at ordinary temperatures.* He used several forms of apparatus, but the one shewn in Fig. 150 was mostly employed. It consisted of the platinum air-thermometer A (which had been previously used by V. Meyer, Lamb and Riddle for their well-known melting point experiments) enclosed in a glass sphere of $\frac{1}{3}$ litre capacity. A stream of water at a constant temperature was maintained through A, whilst the gaseous mixture under investigation was kept in B with a manometer attached so that pressure readings could be made at regular intervals. In one series of experiments (I) the temperature of the surface was not allowed to exceed that of the surrounding gas, so that it was always

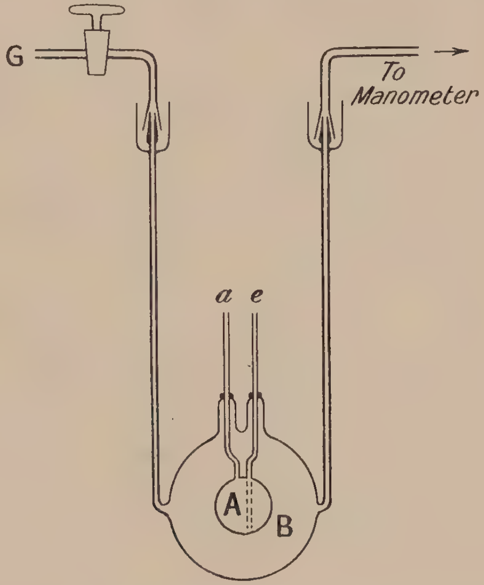

FIG. 150.—BODENSTEIN'S APPARATUS.
(From *Zeit. Physik. Chem.*)

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* *Zeit. physik. Chem.* 46 (1903), pp. 625-776.

covered with a film of water, in another (II) the surface was kept dry by maintaining it at a higher temperature than the surrounding gas.

It was found in Series I that, provided the platinum surface was kept very clean (an essential condition), not only could a rapid rate of combination be observed at so low a temperature as 0° C. with undiluted electrolytic gas, but also that in such circumstances the rate was always proportional to the pressure. In cases where excess of either hydrogen or oxygen was present in the system, the observed rate was much greater but still proportional to the partial pressure of the '*knall-gas*' present. The following results will suffice to illustrate these features:

TABLE CXVI.—BODENSTEIN'S EXPERIMENTS ON THE COMBINATION OF HYDROGEN AND OXYGEN OVER WET PLATINUM AT 0° C. (SERIES I)

(1) *Mixture* $=2H_2+O_2$. $T=0°$.

Time - -	0	2	5	10	15	34 mins.
Pressure -	726	665	577	455	353	122 mm.
k - - -	—	0·0191	0·0199	0·0203	0·0209	0·0227

(2) *Original Mixture* $=2H_2+2O_2$. $T=0°$.

Time - -	0	2	6	10	20 mins.
Pressure -	801	679·8	510	400	265·5 mm.
k - - -	—	0·0499	0·0491	0·0493	0·0514

(3) *Original Mixture* $=8H_2+O_2$. $T=0°$.

Time - -	0	2	6	10	20 mins.
Pressure -	801	746	664·2	613·1	549 mm.
k - - -	—	0·0457	0·0462	0·0453	0·0441

N.B.—The 'k' values are those deduced by an equation of the first order $\left(k=\frac{1}{t}\log\frac{P_0}{P_t}\right)$ from the partial pressure of the undiluted 'knall-gas' $(2H_2+O_2)$ in each case.

These results were explained on the basis of a 'diffusion theory' originally due to Nernst, by assuming an infinitely great rate of combination at the surface, and therefore that the observed rate depends on the rate of solution of the gas in defect in the water film. Thus, it was supposed that when great excess of oxygen is present: "*Dadurch ensteht in der Reactionsphase eine endliche und bald sogar eine dem Verteilungsgleichgewicht entsprechende Konzentration des Wasserstoffs, es kann also jetzt von ihm nur so viel auflösen als durch den gleichzeitig aufgelösten Sauerstoff verbrannt wird, d. h. die Auflösung des Sauerstoffs ist für die Auflösung beider Gase massgebend.*"

Unfortunately, whilst the results of many experiments agreed with this theory, others admittedly did not, and no satisfactory explanation of the discrepancies was afforded, so that the matter was left in a rather indefinite position.* This only serves to shew how really difficult such experiments are, and how easily the unwary might be misled by a particular series of results.

In other experiments, in which the temperature of the platinum surface was kept the same as that of the surrounding gas so that a water-film formed on it, whilst results with *undiluted* electrolytic gas conformed to those required by an equation of the first order, any excess of oxygen in the combining mixture tended first to accelerate and afterwards to retard the catalytic combustion.

When the platinum surface was kept dry by maintaining it at a higher temperature than that of the surrounding gas, so that no water-film formed on it, the absolute rate of combination was much greater than in the first series of experiments, and it no longer conformed to an equation of the first order. Thus, in one experiment with undiluted electrolytic gas the velocity constant, calculated from an equation of the first order, increased from 0·038 to 0·117, or by more than 200 per cent., as the pressure in the apparatus fell from 750 to 24·5 mm. in 14 minutes, and in other similar experiments, such '*k*' values increased by 100 per cent. as follows:

TABLE CXVII.—COMBINATION OF HYDROGEN AND OXYGEN OVER DRY PLATINUM SURFACE (SERIES II) (BODENSTEIN)

Mixture = $2H_2 + O_2$. *Temperature of surface* = 14·9°; *of the gases* = 2·2°C.

Time -	0	1	2	4	6	8	10	12	14 mins.
Pressure -	750	686	623	499	379	270	167	76	24·5 mm.
'k' × 1000	—	38	41	47	50	57	67	86	117

It was also found in such circumstances that, whilst excess of hydrogen had no great influence on the course of the reaction, excess of oxygen accelerated it. Altogether, it was concluded that probably the controlling factor was the solubility of oxygen in platinum, the actual rate of steam formation at the surface being much more rapid. With undiluted electrolytic gas it was thought that the reaction velocity was influenced in a high degree by the outward diffusion of steam or otherwise it would have conformed to an equation of the first order.

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* Thus Bodenstein said, "die erste Versuche, wie das ja häufig der Fall ist, die am besten 'stimmenden' gewesen waren. Bei allen späteren war der Auschluss an die zu Grunde gelegt Gleichung ein merklich schlecterer, und eine ganz Anzahl Beobachtungen wurden gemacht, die zu der Annahme der unendlich grossen Verbrennungsgeschwindigkeit nicht stimmten . . ." (*loc. cit.* p. 737).

In 1905 Bodenstein and Ohlmer published an account of their experiments upon the catalytic combination of carbonic oxide and oxygen over a silica surface at a temperature of about 300°,* from which they concluded that the rate of combination conformed to the equation

$$\frac{dx}{dt}=k\frac{(m+a-x)}{(n+b-x)},$$

where a and b are the initial concentrations of the oxygen and carbonic oxide respectively, and m $(=140)$ and n $(=45)$ are constants. Thus it seemed as though the carbonic oxide had retarded its own combustion in such circumstances. This peculiarity was not, however, observed when the catalysing surface was either quartzite or rock-crystal. For, in both these cases the observed reaction velocity was directly proportional to the CO-concentration, and inversely (though roughly only) to the square root of the O_2-concentration.

In 1907 Bodenstein and Fink published experiments upon the Kinetics of the Sulphuric Acid Contact Process,† in which it was shewn that when mixtures of sulphur dioxide and oxygen react over platinum gauze at temperatures between 150° and 250° C., the rate of combination is directly proportional to the SO_2-concentration, independent of the O_2-concentration (except when it is very small), but inversely proportional to the square root of the SO_3-concentration in the system. Indeed, the course of the reaction could be represented by the equation :

$$\frac{dx}{dt}=k\frac{(a-k)}{x^{\frac{1}{2}}},$$

where a = initial SO_2-concentration, and x = the amount which has undergone change up to time t.

This result was explained on the supposition that the actual rate of combination of the two reactants in question at the platinum surface was infinitely great compared with their rates of diffusion on to it ; and seeing that to reach the surface they had to pass through an adsorbed layer of sulphur trioxide, it was the rate of diffusion by the slower moving gas (SO_2) through this which really determined the rate of combination.

Considered as a whole, and so far as they were free from admitted irregularities, Bodenstein's experiments may be said to have directed attention to the importance of 'adsorption' and 'diffusion' factors in catalytic combustion. Bodenstein himself was led to distinguish between two limiting cases, namely, (1) on the one hand, those in which the chemical union of the reactants at the surface proceeds at an infinitely faster rate than the operation of any other factor involved in the process, and (2) on the other, those in which the actual rate of combination of the reactants at the surface is the slowest of all the factors concerned.

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* *Zeit. physik. Chem.* 53 (1905), p. 166.

† *Zeit. physik. Chem.* 60 (1907), pp. 1 to 45.

Nernst's Diffusion Theory

In this connection it should be mentioned that when in 1904 W. Nernst enunciated his general '*Theorie der Reaktionsgeschwindigkeit im heterogenen System*,'* in which the controlling importance of diffusion factors was emphasised, he included 'catalytic reactions' as a special case, saying that, whenever it can be assumed that the catalysing surface remains unchanged, and that the surface-reaction proceeds with a practically infinite velocity, the observed reaction velocity will generally be determined by diffusion factors. Thus, to quote his words, "*Da diese Reaktionen wohl ausschliesslich an der Grenzfläche des Katalysators sich abspielen, so wird die Geschwindigkeit keineswegs durch den Mechanismus der betreffenden Reaktion, sondern wenn, was allerdings von vornherein nicht sicher ist, der Katalysator während des Reaktionsverlaufes konstante Beschaffenheit behält und zugleich mit praktisch unendlicher Geschwindigkeit die betreffenden Substanzen an der Grenzfläche zur Reaktion bringt, auch hier lediglich durch die Diffusion der reagierenden Stoffe zum Katalysator bedingt werden.*"

And, doubtless, in cases where the postulated conditions are fulfilled, and no others supervene, the observed velocity would be governed by 'diffusion factors'; but, in surface combustion, such is not usually the case, owing to 'activation' of reactants supervening.

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* *Zeit. physik. Chem.* **47** (1904), p. 52.

CHAPTER XXXV

RESEARCHES ON CATALYTIC COMBUSTION AT TEMPERATURES BELOW INCANDESCENCE (1905 TO 1926)

DURING the past twenty-five years the catalytic combustion of hydrogen and carbonic oxide at temperatures below incandescence has been extensively studied by W. A. Bone with various collaborators, first of all at Manchester University, then at the University of Leeds, and finally at the Imperial College, London, where the work is still being continued.

In conjunction with R. V. Wheeler were published (in 1906) the results of experiments upon the "Combination of Hydrogen and Oxygen in Contact with Hot Surfaces,"* and during the past two years those of similar experiments upon carbonic oxide and oxygen, made at various times conjointly with G. W. Andrew, A. Forshaw, H. Hartley, A. Appleyard, W. A. Haward, S. Robson, A Whittaker, and D. S. Chamberlin, have appeared.† They will now all be reviewed together as briefly as possible, leaving readers who are sufficiently interested in them to refer to the original memoirs for details.

Scheme of Research. At the outset of the research the necessity of taking as wide a view as possible of the phenomena was realised; accordingly it was decided to examine in detail the action of a great variety of surfaces, including porous porcelain, fire-clay, magnesia, platinum, gold, silver, nickel, copper, and easily reducible oxides such as those of copper, nickel, iron and manganese, in each case at some suitable temperature well below the ignition point of the gaseous mixture under investigation. And in dealing with easily oxidisable metals or reducible oxides, care was taken to distinguish between the purely catalytic combination of the reacting gases without any permanent oxidation or reduction of the surface and processes which do involve such changes. For it is important that the essential difference between the two kinds of actions (*e.g.* between the combination of electrolytic gas in contact with a copper oxide surface, and the mere reduction of such a surface by hydrogen) should be clearly borne in mind in all discussions upon the subject, otherwise serious confusion of thought will arise. Fortunately in such cases it is usually not difficult

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* *Phil. Trans. Roy. Soc. A.* **206** (1906), pp. 1-75.

† *Proc. Roy. Soc. A.* 109 (1925), 459; **110** (1926), 16; **112** (1926), 474; and **114** (1927), 169.

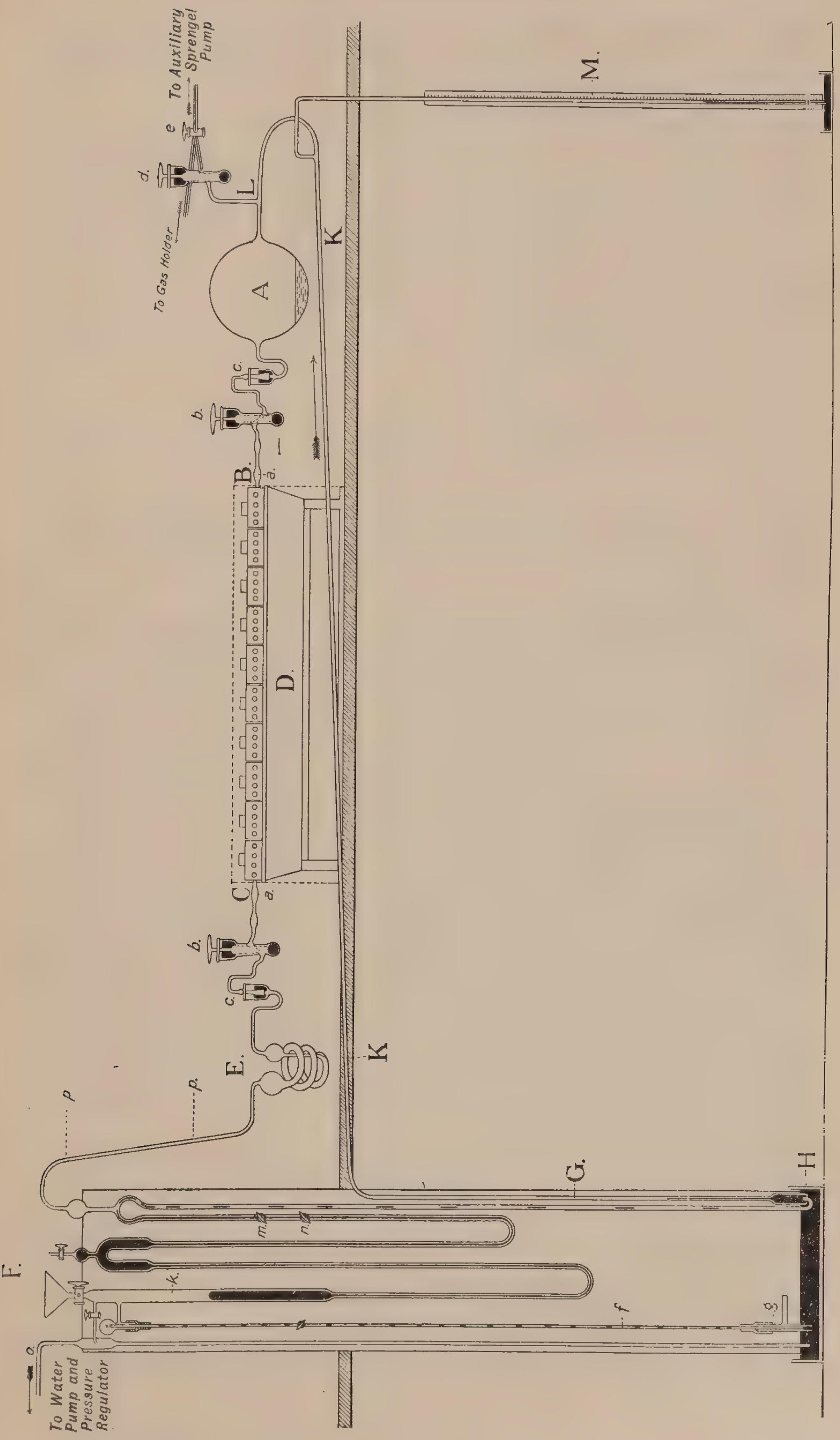
To Auxiliary Sprengel Pump
e
d.
To Gas Holder
L
A
K
M.
c.
b.
B.
a.
D.
C
a.
b.
c.
E.
p.
p
K
G.
H
F.
k.
m.
n.
f
g
o.
To Water Pump and Pressure Regulator

FIG. 151.—CIRCULATION APPARATUS.

to find some range of temperature within which the purely catalytic process goes on uncomplicated by the other; and it is the former alone which now concerns us.

In the cases of both hydrogen-oxygen and carbonic oxide-oxygen mixtures systematic experiments were made with (*a*) the reactants present in their combining proportions, and (*b*) with one or other of them in excess. Also, the effects of previously exposing the surface at the experimental temperature to one or other of the reactants were always studied, with significant results so far as the theory of the catalytic process is concerned. In one or two cases, temperature coefficients were determined. Finally, the effects of progressively drying-out a $2CO + O_2$ system undergoing catalytic combustion were studied.

Another feature of the work has been that throughout each given series of experiments, which often extended over many weeks or even months continuously, not only was the temperature of the surface kept constant, but also its condition and behaviour kept under continuous close observation from first to last, so that its whole history was ascertained, a circumstance which experience has shewn to be highly important for the correct interpretation of results.

The Circulation Apparatus and Method. For the great majority of the experiments, the circulation apparatus devised by Bone for studying the slow combustion of hydrocarbons was employed. Fig. 151 shews it in the form used for investigating the catalytic union of hydrogen and oxygen over hot surfaces, and although it had to be modified in detail from time to time to suit the requirements of later experiments with carbonic oxide and oxygen, the principle of it remained unaltered.

It consists essentially of a closed system in which the reacting gases are circulated, at a uniform rate, over the particular surface under investigation, maintained at a constant temperature, and afterwards through some cooling or absorption arrangement to ensure the rapid removal of the reaction product. The rate of combination is measured by observing the pressure in the apparatus at regular intervals of time. By means of a series of 'bye-passed' sampling tubes (Fig. 152), samples of the gases can, if necessary, be cut off at intervals during an experiment without altering the pressure in the apparatus, or in any way interfering with either the course or the conditions of the reaction.*

Two great advantages are claimed for this apparatus, namely that (1) it allows of velocity measurements being made in a single experiment over a wide range of pressure (from about 600 mm. to as low as 20 mm.), and (2) in cases where the gases are not originally present in their combining ratio, it is possible to follow the variations of the velocity with an ever increasing excess of one of them.

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* Whenever such 'bye-passed' sampling tubes were included in the circuit, they were sealed into the apparatus between the points *p*, *p*, shown in Fig. 151.

The glass globe *A* (capacity = about 1200 c.c.) serves merely as a reservoir for the reacting gases; it ordinarily contains a few cubic centimetres of distilled water, so that the gases are kept saturated with aqueous vapour at the room temperature (as indicated by a thermometer placed with its bulb in contact with the outer wall of the globe), though when 'dry' systems are being investigated, some suitable drying agent may be substituted.

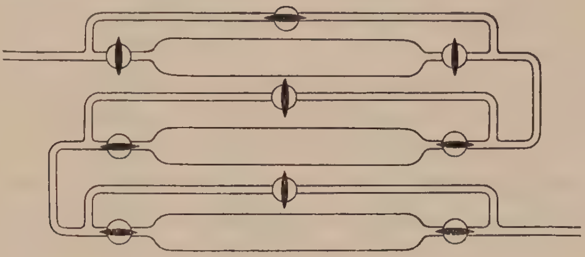

FIG. 152.

From the globe the gases are drawn by the automatic Sprengel pump *F* (the 'circulating pump'), at a uniform rate, through the Jena hard glass combustion tube *BC*, containing the surface under examination, which is heated in the constant temperature furnace *D*. This furnace is protected from draughts by a thick asbestos hood (indicated by dotted lines in the diagram), at each end of which are arranged suitable screens in order to shield the rest of the apparatus from radiated heat. The gas supply of the furnace is regulated by a governor, which keeps the temperature constant for, if necessary, many days together.

Each end of the combustion tube is fitted with special glass joints *aa* composed of rings of glass of gradually diminishing hardness fused together, ending in a grade of glass soft enough to allow of its being fused direct on to the mercury cup taps *bb*. The adoption of these special joints obviate the use of any indiarubber connections in the apparatus. The mercury cup taps *bb*, are in turn connected, by fused glass joints, with the ground glass joints *cc*, each of which works under a mercury seal.

On leaving the combustion tube the gases pass through a glass worm *E*, surrounded by a water jacket (not shewn in the diagram), through which a stream of cold water is constantly maintained, to ensure the rapid cooling of the hot gases and the condensation of steam. The cooled gases then pass onwards to the automatic Sprengel pump *F*, which delivers them up into the vertical tube *G*, standing over mercury in the trough *H*; thence they pass along the horizontal tube *KK*, back again into the globe *A*, thus completing the circuit.

The apparatus is closed by the mercury cup tap *d*, sealed into the T-piece *L*. The other side of *d* is connected, by a fused glass joint, with the three-way tap *e*, through which communication may be made either with the gas-holder containing the experimental mixture, or with an auxiliary pump used for the rapid exhaustion of the apparatus, as circumstances require. The pressure in the apparatus at any given moment is indicated by the mercurial gauge *M*, fused into the horizontal tube *KK* at a point near to the globe *A*.

It is necessary for the complete success of a given series of experiments that the rate of circulation shall be maintained substantially uniform for, if need be, many days together. This may be secured by automatically regulating the suction of the water pump employed to work the Sprengel circulating pump.

The capacity of the whole apparatus is about 1500 c.c., that of the combustion tube only about 75 to 125 c.c., according to the closeness with which it is packed with the catalysing material. In considering the experimental results, it is useful to remember that the dimensions of the apparatus are such that a fall in pressure of, say, x millimetres during a given time interval corresponds to the combination of as nearly as possible $2x$ cubic centimetres of the reacting gases ($2H_2 + O_2$ or $2CO + O_2$).

Such then are the usual arrangements when a 'moist' system is being investigated; they can, however, easily be adapted for the investigation of a 'dry' system, by replacing the water in *A* by some suitable drying agent, and inserting other 'drying' devices in the circuit. In extreme cases, in addition to the inclusion of P_2O_5-drying tubes at suitable points, glass spirals cooled by immersion in baths of liquid air are inserted immediately *before* and *after* the reaction tube *D*. Fig. 153 shews diagrammatically the apparatus as installed for the investigation of the behaviour of a rigidly dried $2CO + O_2$ mixture in contact with silver and gold surfaces. Here S = the surface in the reaction tube *AA* maintained at the desired temperature in the furnace *BB*, C_1 and C_2 are hard-to-soft glass joints, D_1 and D_2 mercury sealed glass stop-cocks, N_1 and N_2 glass spirals or tubes each immersed in a liquid air bath. K_1 to K_4 are P_2O_5-drying tubes, E_1 and E_2 are absorption towers containing a specially prepared mixture of soda-lime with three times its weight of quicklime. *F* marks the position of the automatic Sprengel circulating-pump, whilst *M* and *G* are the capacity-vessel and manometer respectively.

Experimental Results. To summarise adequately the results of the vast number of experiments which have been made during the twenty-five years already covered by the research is not altogether easy, because, whilst as a rule the behaviours of most of the surfaces examined shewed many common features, each surface had its peculiarities in that it either exhibited such features in a specially marked degree, or disclosed some new one. All that can be attempted is to give the reader a general view of the principal results, leaving him to glean the rest from original papers.

The temperature at which the various surfaces became reasonably 'active' towards the gaseous systems examined, naturally differed very greatly. As might be expected, platinum was by far the most active,

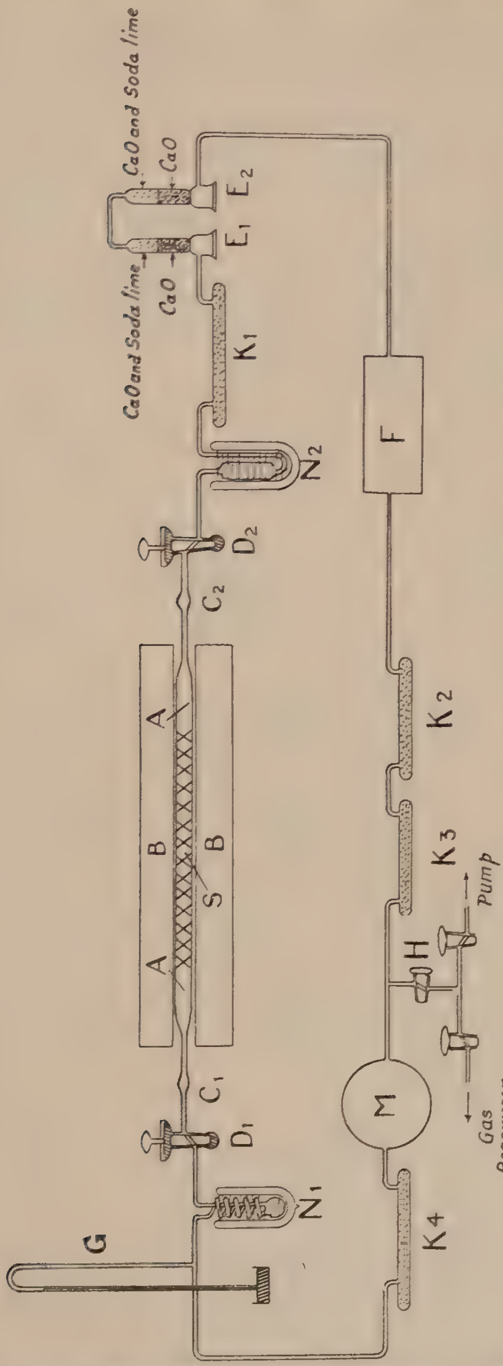

FIG. 153.—THE CIRCULATION APPARATUS AS ARRANGED FOR THE STUDY OF CATALYTIC COMBUSTION IN 'DRY' SYSTEMS.

and it was the most difficult to keep under control. Of the other metals, gold was found to be reasonably active between 250° and 300°, silver between 400° and 500°, copper between 135° and 250°, and nickel between 220° and 365°, according to the gaseous mixture employed. Easily reducible oxides, such as nickel and copper oxides, could be used with effect at such low temperatures as 150° to 200° even. Non-reducible surfaces such as porous porcelain or magnesia required a temperature between 430° and 500°. With the exception of copper and its oxide, a rather lower temperature was required for a given surface to catalyse a moist hydrogen-oxygen than a moist carbonic oxide-oxygen mixture with equal effect, although nickel oxide acted about equally well with each mixture at 150°. Singularly enough, nickel gauze catalysed an electrolytic gas mixture much more powerfully than it did a moist $2CO + O_2$ mixture at the aforesaid temperatures.

In two important respects the behaviour of *all* the surfaces examined towards either electrolytic gas or a moist $2CO + O_2$ mixture was always alike within the aforesaid temperature ranges in that: (1) the catalysing power of a new surface always increased up to a certain steady maximum when successive charges of the gaseous mixtures were circulated over it, and (2) after the attainment of such steady state, the rate of combination of the gases was invariably proportional to the pressure, or, in other words, the combustion always simulated a reaction of the first order.

Another respect in which most of the surfaces agreed was that, when either of the reacting gases was present in excess, the rate of combination was proportional (or very nearly so) to the partial pressure of the combustible gas (*i.e.* hydrogen or carbonic oxide as the case might be), which thus became the determining factor in each case. This applied to the catalysing actions of porcelain, fireclay, magnesia and gold towards both hydrogen-oxygen and carbonic oxide-oxygen mixtures; also to those of nickel, copper and copper-oxide towards CO-oxygen mixtures, and to those of nickel oxide and platinum towards H_2-oxygen mixtures. In only two cases, namely those of nickel oxide towards CO-oxygen mixtures and of copper oxide towards H_2-oxygen mixtures, was the rate of combination in such circumstances mostly controlled by the partial pressure of the oxygen.* Silver behaved rather exceptionally in this respect in that the rate appeared controllable by the partial pressure of *either* the combustible gas *or* of the oxygen, *or* of neither, according to circumstances which were definitely reproducible at will.

It was also discovered that whereas in nearly all cases (except those of reducible oxides) previous exposure of a surface (in a normal state of activity) to the combustible gas (hydrogen or carbonic oxide as the case might be) at the experimental temperature stimulated its catalysing power in a most remarkable degree, similar exposure to oxygen either depressed it, or had no appreciable effect. The catalysing power of a gold surface towards CO-oxygen mixtures was, however, stimulated by previous exposure to either oxygen or carbonic oxide, there being evidence of the stimulus thus imparted being due to deeply 'occluded' gas in each case. In the case of only one other surface, namely that of copper oxide was evidence forthcoming of such an oxygen-stimulation.*

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* In the first named case the 'oxgyen-control' was less marked than in the latter, where it was complete.

In illustration of some of the points referred to in the preceding paragraph, a few typical examples may be cited.

TABLE CXVIII.—COMBINATION OF HYDROGEN-OXYGEN MIXTURES OVER A POROUS PORCELAIN SURFACE AT 430° C. (BONE AND WHEELER)

(*a*) *Electrolytic Gas with Surface in 'Normal' Condition.*

t.	$P_{2H_2+O_2}$.	k_1.
Hours.	mm.	
0	411·8	—
2	343·3	0·0395
4	283·5	0·0405
6	230·3	0·0420
8	188·5	0·0424
10	155·6	0·0422
12	126·2	0·0424
14	106·0	0·0422

(*b*) *Original Mixture* = $3H_2 + O_2$ *nearly.*

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
Hours.	mm.	mm.	mm.		
0	411·8	311·8	100·0	—	—
2	314·2	246·7	67·5	0·0509	0·0853
4	243·4	199·5	43·9	0·0485	0·0894
6	184·9	160·5	24·4	0·0481	0·1021
8	144·2	133·4	10·8	0·0461	0·1208
10	117·4	115·5	1·9	0·0431	0·1721

(*c*) *Original Mixture* = $H_2 + O_2$ *nearly.*

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
Hours.	mm.	mm.	mm.		
0	398·0	196·0	202·0	—	—
2	358·0	169·2	188·8	0·0320	0·0148
4	329·5	150·2	179·3	0·0289	0·0130
6	294·0	126·5	167·5	0·0317	0·0136
8	268·4	109·5	158·9	0·0316	0·0131
12	228·3	82·7	145·6	0·0312	0·0119
24	156·9	35·1	121·8	0·0311	0·0092
28	142·1	25·3	116·8	0·0318	0·0085
32	129·0	16·5	112·5	0·0335	0·0080

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* It should be understood that these statements, and all others, regarding the investigations in question, apply to the particular temperature and other experimental conditions in each case.

(*d*) *Shewing Effects of Previous Exposure to Hydrogen or Oxygen at 430° C. upon the Catalysing Power of the Surface towards* $2H_2+O_2$ *Mixtures.*

	k_1	
Initial ‘ normal ’ value	0·036	Successive Experiments $T=430°$.
After 24 hours exposure to H_2	0·051	
,, 24 ,, ,, O_2	0·030	
,, 40 ,, ,, H_2	0·059	
,, 48 ,, ,, O_2	0·037	
,, 72 ,, ,, H_2	0·062	

TABLE CXIX.—COMBINATION OF HYDROGEN-OXYGEN-MIXTURES OVER GOLD GAUZE AT 250° (BONE AND WHEELER)

(*a*) *Electrolytic Gas with Surfaces in ‘ Normal ’ Condition.*

t	0	1	2	3	4	5	6	7 hours
Pressure	355·5	275·5	215·8	175·8	141·1	112·2	89·3	70·1 mm.
k_1	—	0·1107	0·1084	0·1019	0·1003	0·1001	0·1000	0·1007

(*b*) *Original Mixtures* $=H_2+2O_2$ *nearly.*

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
Hours.	mm.	mm.		
0	116·6	244·1	—	—
1	85·0	228·4	0·1374	0·0289
2	65·0	218·3	0·1269	0·0242
3	52·3	212·0	0·1161	0·0204
4	43·6	207·6	0·1068	0·0176
5	37·8	204·7	0·0979	0·0153
6	30·8	201·4	0·0964	0·0139
8	19·9	195·7	0·0960	0·0120
10	14·4	192·9	0·0908	0·0102

(*c*) *Original Mixture* $=3H_2+O_2$ *nearly.*

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
Hours.	mm.	mm.		
0	295·7	95·0	—	—
1	251·1	72·8	0·0709	0·1156
2	210·9	52·6	0·0734	0·1283
3	177·8	36·0	0·0736	0·1404
4	150·3	22·4	0·0735	0·1569
5	127·1	10·7	0·0733	0·1897
6	113·7	3·9	0·0692	0·2311

(*d*) *Electrolytic Gas after Exposure of Surface to Hydrogen at 250° for Four Days.*

t - -	0	½	1	1½	2	2½	3	4 hours
Pressure -	324·6	257·3	212·8	182·0	157·3	138·9	125·9	103·1 mm.
k_1 - -	—	0·2018	0·1834	0·1674	0·1573	0·1474	0·1371	0·1245

TABLE CXX.—COMBINATION OF MOIST CARBONIC OXIDE-OXYGEN MIXTURES OVER A FIRECLAY SURFACE AT 490° (BONE AND ANDREW)

(*a*) $2CO + O_2$ *Mixture with Surface in 'Normal' Condition.*

t - -	0	2	4	6	10 hours
Pressure	408	380	355	331	287 mm.
k_1 - -	—	0·0154	0·0151	0·0151	0·0153

(*b*) *Original Mixture* $= 4CO + O_2$ *nearly.*

t.	P_{CO}.	P_{O_2}.	$k_{1_{CO}}$.	$k_{1_{O_2}}$.
Hours.	mm.	mm.		
0	299	76	—	—
2	246	49	0·0427	0·0953
4	207	29	0·0400	0·1046
6½	167	9	0·0390	0·1425

(*c*) $2CO + O_2$ *Mixture after Exposure of Surface at 490° to Residual Gas from* (*b*) *for 48 hours.*

t - - - -	0	2	4 hours
Pressure - -	400	237	150 mm.
k_1 - - - -	—	0·1137	0·1065

(*d*) *Original Mixture* $= CO + O_2$ *nearly.*

t.	P_{CO}.	P_{O_2}.	$k_{1_{CO}}$.	$k_{1_{O_2}}$.
Hours.	mm.	mm.		
0	201	200	—	—
1	157	178	0·1073	0·0506
2	126	162	0·1014	0·0457
4	85	142	0·0934	0·0372
10	19	109	0·1024	0·0263

(*e*) $2CO_2 + O_2$ *Mixture after Prolonged Treatment of Surface with Oxygen at 490°.*

t - -	0	5	24	42 hours
Pressure -	400	334	165	80 mm.
k_1 - -	—	0·0157	0·0160	0·0167

TABLE CXXI.—COMBINATION OF MOIST CARBONIC OXIDE-OXYGEN MIXTURES OVER GOLD GAUZE AT 300° C. (BONE AND ANDREW)

(a) $2CO + O_2$ *Mixture with Surface in Normal Condition.*

t - -	0	1	2	2½ hours
Pressure -	430	228	119	84 mm.
k_1 - -	—	0·275	0·279	0·283

(b) *Original Mixture* $= CO + O_2$ *nearly.*

t.	P_{CO}.	P_{O_2}.	$k_{1_{CO}}$.	$k_{1_{O_2}}$.
Hours.	mm.	mm.		
0	191·3	198	—	—
1	77·5	141	0·3924	0·1475
1½	49·4	127	0·3926	0·1286
2	32·1	118	0·3876	0·1124
2½	20·3	112	0·3896	0·0989
3	14·1	109	0·3775	0·0864

(c) $2CO_2 + O_2$ *Mixture after Exposure of Surface at 300° to Residual Oxygen from* (b).

t - -	0	½	1	1½ hours
Pressure -	380	156	48	16 mm.
k_1 - -	—	0·773	0·898	0·907

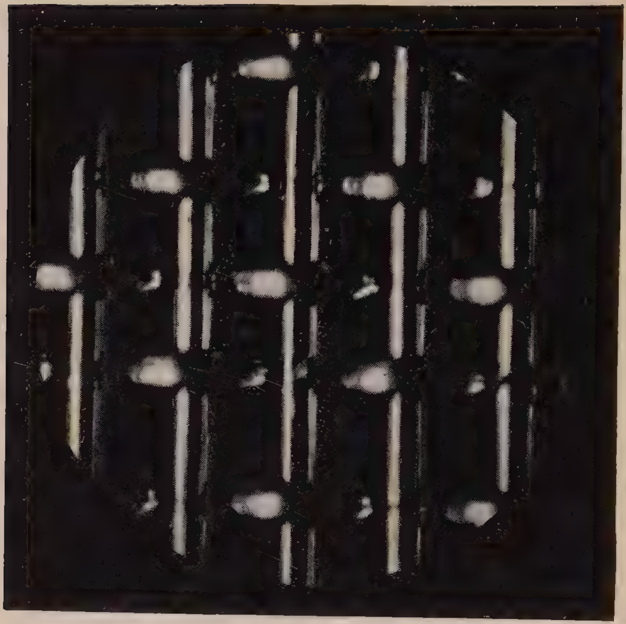
(d) *Original Mixture* $= 4CO + O_2$ *nearly.*

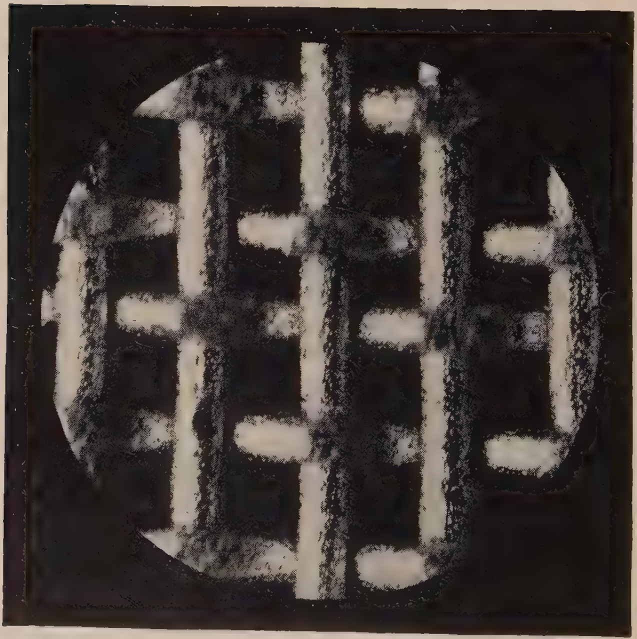
t.	P_{CO}.	P_{O_2}.	k_{CO}.	k_{O_2}.
Hours.	mm.	mm.		
0	310	76	—	—
0·5	267	54	0·1300	0·2968
1	224	33	0·1412	0·3623
1·5	195	19	0·1343	0·4014
2	169	5	0·1317	0·5866

(e) $2CO + O_2$ *Mixture after Exposure of Surface at 300° for 72 Hours to Residual Gas from* (d) *followed by Rapid Evacuation of Apparatus.*

t - -	0	¼	½	1 hour
Pressure -	398	307	170	42 mm.
k_1 - -	—	0·4512	0·7390	0·9767

PLATE XXX.





Photomicrographs of Silver Gauze used in Surface Combustion Experiments.

The Relative Catalysing Powers of a Porcelain Surface at 500° C. towards Mixtures of Various Combustible Gases and Oxygen

As might be expected, a hot surface does not accelerate the combustion of all gases alike; indeed it often acts selectively. As a rule, the combustion of hydrogen is induced more powerfully than that of carbonic oxide, and both gases are usually much more amenable to the catalytic process than is methane, which proves that combustion in contact with hot surfaces is a phenomenon distinct from that in flames, where methane and hydrocarbons generally are more readily burnt than hydrogen. Having dealt with the latter point in Chapter XXXI, we will now, for purposes for comparison give the following data in illustration of the former:

TABLE CXII.—BEHAVIOUR OF (*a*) AN H_2+CO+O_2 MIXTURE AND (*b*) A $CH_4+2H_2+O_2$ MIXTURE IN CONTACT WITH POROUS PORCELAIN AT 500° C. (BONE AND FORSHAW)

(*a*)

t.	Partial Pressures of		
	H_2.	CO.	O_2.
Hours.	mm.	mm.	mm.
0	147	143	150
3½	33	118	80
6½	8	53	34

(*b*)

t.	Partial Pressures of		
	CH_4.	H_2.	O_2.
Hours.	mm.	mm.	mm.
0	101·3	203·0	97·5
7	96·5	27·2	0·8
Gas burnt	4·8	175·8	96·7

Photographic Evidence of Gas-Occlusion during Catalytic Combustion

In view of the much debated question of whether catalytic combustion depends on the 'activation' of the *adsorbed* gases only, or whether (as we think) more deeply occluded gases are also involved, attention is directed to the two photomicrographs shewn in Plate XXX. The upper one is a piece of pure assay-silver gauze as it appeared at the outset of a series of six experiments, extending over nine days, in which it was used to induce the union of hydrogen and oxygen at 400° C., and between some of which experiments it had been exposed also to either hydrogen or oxygen at the reaction temperature for 18 or 36 hours respectively. At the end of the experiments, no change in its outward appearance could be detected by the eye; but on heating it momentarily to dull redness, it suddenly developed the beautiful frosted appearance shewn in the lower photomicrograph, and lost all its pristine elasticity. Indeed it became exceedingly brittle. There could be little doubt but that this marked change was due to the escape from it of gases occluded in the previous experiments.

Stimulation of the Catalysing Power of Surfaces by previous long Exposure to Hydrogen (or Carbonic Oxide)

The way in which the catalysing power of most of the surfaces concerned could be stimulated by previous exposure to hydrogen, is well illustrated by the curves shewn in Figs. 154 and 155 which shew the rates at which moist electrolytic gas combined (*a*) over a piece of pure assay-silver foil

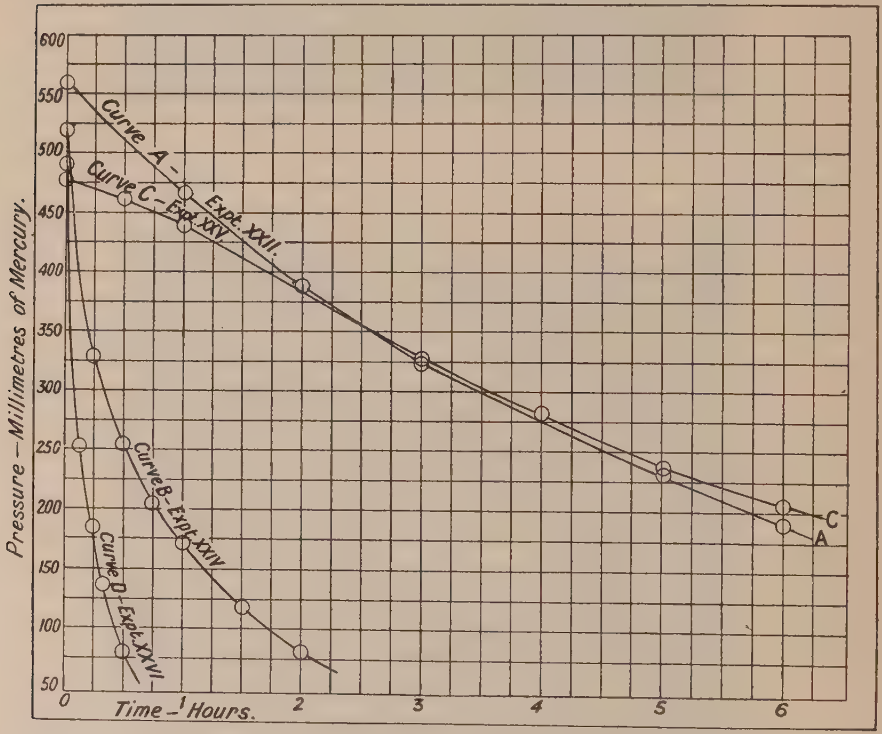


FIG. 154.—EXPERIMENTS WITH SILVER FOIL. PRESSURE CURVES FOR NORMAL ELECTROLYTIC GAS.

Curve **A**, surface in "normal" condition.
,, **B**, surface "hydrogenised" at 400°.
Curve **C**, surface "dehydrogenised" by oxygen.
,, **D**, surface "hydrogenised" at 650°.

at 400° or (*b*) over a piece of gold gauze at 250°, when each surface was *either* in its ‘ normal ’ state of activity *or* in a definitely ‘ hydrogenised ’ state after previous prolonged exposure at some selected temperature to hydrogen. Such enhanced ‘ catalysing power ’ was attributed by Bone and Wheeler to direct effects of occluded hydrogen, and much other evidence could be cited in support of such view. On the other hand

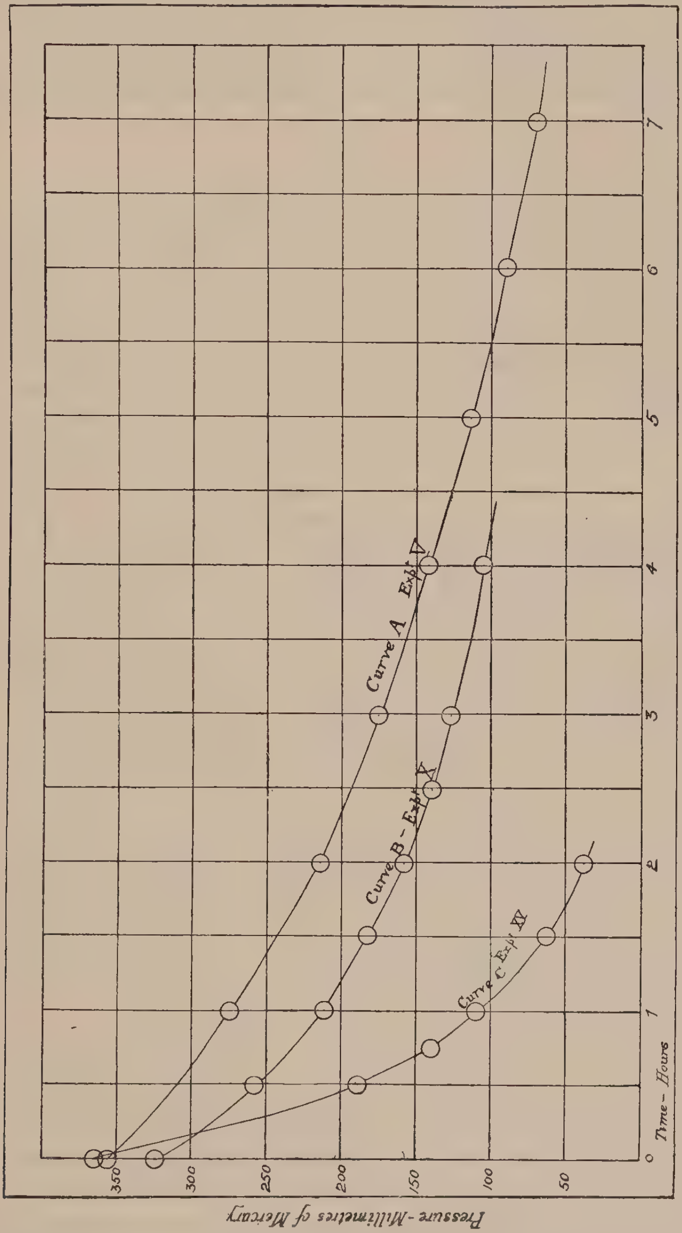


FIG. 155.—EXPERIMENTS WITH GOLD GAUZE. PRESSURE CURVES FOR NORMAL ELECTROLYTIC GAS.

Curve **A**, surface in “ normal ” condition. Curve **B**, surface “ hydrogenised ” at 250°. Curve **C**, surface “ hydrogenised ” at 600°.

D. L. Chapman, who confirmed experimentally the 'effects' referred to, has suggested recently that it can be better explained on the supposition of the removal of an inhibiting oxygen film. It is not easy to decide between the two views, although against the latter may be cited the fact that the catalysing power of gold towards moist $2CO + O_2$ mixtures at 300° can be stimulated by previous exposure to *either* oxygen *or* the combustible gas. Also it would hardly seem to explain so well the marked stimulation of such surfaces as porous porcelain by hydrogen.

Experiments with Easily Reducible Oxides (CuO, NiO, *etc.*)

Very remarkable evidence was obtained not merely (1) that the true catalytic combination of hydrogen-oxygen or carbonic oxide-oxygen mixtures in contact with such surfaces as the oxides of nickel and copper at the temperatures examined involves no permanent oxidation or reduction of the surface, but also (2) that it is primarily due to the formation at the surface of an adsorbed film of active oxygen, which may be more or less effective than the oxygen actually combined with the metal (as NiO or CuO) in burning the combustible gas at the same temperature. Whilst oxygen as NiO was much less effective, oxygen as CuO proved to be much more so than the adsorbed O-film, in burning the combustible gas.

This very important point is well illustrated by the following comparative experiments made by Bone and Wheeler (*loc. cit.* pp. 59 to 67) in which mixtures of $2H_2 + O_2$ and $2H_2 + N_2$, respectively, were circulated over each of the oxides in question at a suitable temperature.

(1) *Experiments with Granular Nickel Oxide.* (Bone and Wheeler.)

(*a*) *With* $2H_2 + O_2$ *Mixture.* $T = 160°\ C.$

t - - -	0	½	1	2	3	4 hours
Pressure -	453·1	430·6	359·3	286·3	227·9	181·7 mm.
k - - -	—	0·1070	0·1007	0·0997	0·0995	0·0992

Then, without any alteration in the surface or other conditions, the following experiment was immediately tried.

(*b*) *With* $2H_2 + N_2$ *Mixture.* $T = 160°\ C.$

t - - -	0	½	1	1½	2 hours
Pressure -	460·3	444·3	436·3	431·3	427·8 mm.
P_{H_2} - -	299·3	283·5	275·5	270·5	267·0
k_{H_2} - -	—	0·0464	0·0354	0·0286	0·0243

It is thus seen that on substituting nitrogen for oxygen in the combining gases the rate at which the hydrogen was oxidised was greatly diminished, shewing that the oxygen as NiO was much less effective than the absorbed O-film in burning the hydrogen.

(2) *Experiments with Copper Oxide.* $T=214°$ *C.* (Bone and Wheeler.) Here the opposite effect is seen, namely that oxygen as CuO is much more effective in burning the hydrogen than is the absorbed O-film formed when electrolytic gas is circulated over the surface. Indeed in the latter case, the catalytic combustion involves the condensation of an O-film on the surface which, though much more active than the O_2 molecules in the surrounding atmosphere, is far less than the oxygen chemically combined as CuO at the surface.

(*a*) *With a* $2H_2+O_2$ *Mixture.* $T=214°$ *C.* (CuO *surface freshly oxidised*).

t - - -	0	1	2	3	4	5 hours
Pressure -	364·5	316·1	257·0	195·4	151·4	111·6 mm.
k_1 - -	—	0·0619	0·0759	0·0912	0·0964	0·1028

Then, after re-oxidising the surface to ensure its being in its original condition, but without altering the temperature, the following experiment was immediately tried.

(*b*) *With* $2H_2+N_2$ *Mixture.* $T=214°$ *C.*

t - -	0	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{2}{3}$	1	$1\frac{1}{2}$ hours
Pressure -	395·7	313·2	248·2	207·6	183·1	162·8	141·4 mm.
P_{H_2} -	263·8	181·3	116·3	75·7	51·2	30·9	9·5
k_{H_2} - -	—	0·977	1·067	1·084	1·068	0·931	0·962

The remarkable difference between the results of these two experiments is brought out by the two curves for the partial pressures of the hydrogen shewn in Fig. 156 ; indeed, merely by substituting inert nitrogen for the oxygen of electrolytic gas, the rate of combustion of the hydrogen was increased something like seven-fold, a fact which seems irreconcilable with the idea of the catalytic combustion involving a rapidly alternating series of reductions and re-oxidation of the surface.

Further comparative experiments were made at 200° with a surface of granular copper oxide which had previously been heated to dull redness in a current of air for 6 hours and afterwards in a stream of oxygen for 12 hours longer. The following two experiments were then made (*a*) with normal electrolytic gas ($2H_2+O_2$), and (*b*) with a mixture $2H_2+N_2$, the temperature (200° C.) and other experimental conditions being the same in each case. It will be seen, from the results shewn in Table CXXIII, that whereas only 9·7 per cent. of the original hydrogen was burnt during the first hour in (*a*) no less than 50 per cent. of it disappeared in (*b*) when nitrogen was substituted for the oxygen of electrolytic gas.

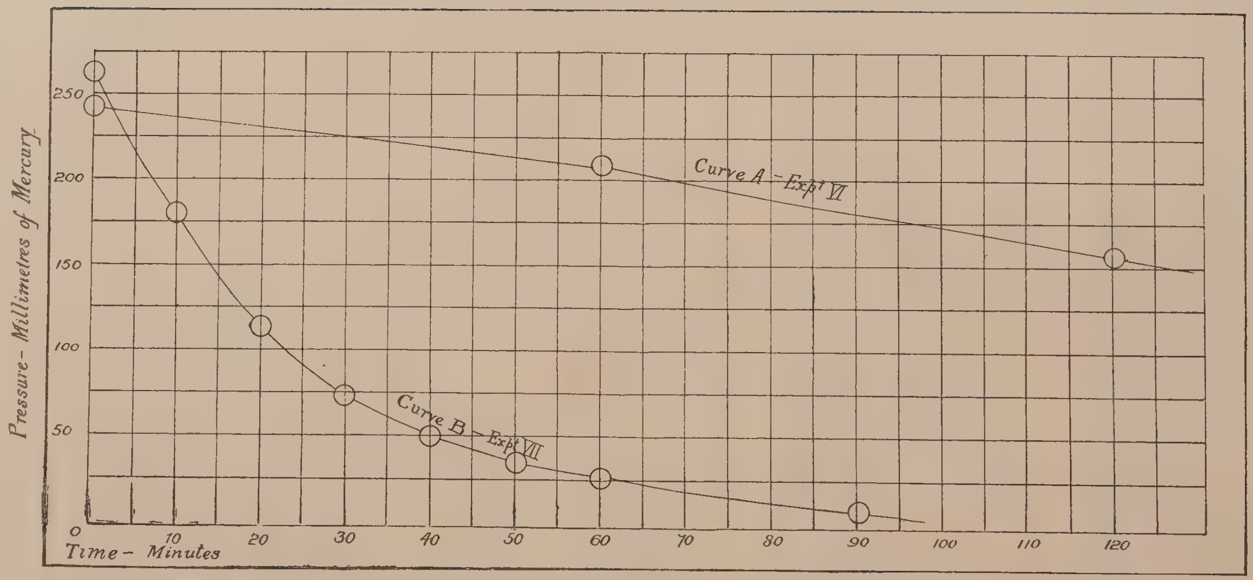


FIG. 156.—EXPERIMENTS WITH COPPER OXIDE SURFACE AT 214° C. PARTIAL PRESSURES OF HYDROGEN.

Curve **A**, for $2H_2+O_2$. Curve **B**, for $2H_2+N_2$.

TABLE CXXIII.—EXPERIMENTS WITH COPPER OXIDE (BONE AND WHEELER)

(a)				(b)			
Original Mixture $=2H_2+O_2$. $T=200°$ C.				Original Mixture $=2H_2+N_2$. $T=200°$ C.			
	t.	Pressure.	k_1.	t.	Pressure.	P_{H_2}.	k_{H_2}.
	Hours.	mm.		Hours.	mm.	mm.	
No permanent reduction of the copper oxide $H_2/O_2=2·0$.	0	488·8	—	0	333·5	210·7	—
	1	441·7	0·0440	1	226·0	103·2	0·3100
	2	399·1	0·0440	2	162·3	38·5	0·3690
	3	360·0	0·0443	3	131·9	8·1	0·4720
$H_2/O_2=1·82$.	4	319·0	0·0465				
	5	284·5	0·0470				
	6	242·0	0·0509				
$H_2/O_2=1·47$.	8	169·5	0·0575				
	10	120·3	0·0608				
	11	97·8	0·0636				

Another significant circumstance to be noted in the above connection was that in (*a*) so long as the pressure remained fairly high there was no permanent reduction of the surface, the H_2/O_2 ratio in the gaseous medium remaining at 2·0; by the end of the sixth hour, however, the ratio had fallen to 1·82, indicating some incipient reduction, and at the end of the experiment it was 1·47 only. This shews that at first the ' active ' O-film condensed on the surface actually protected the underlying CuO from the attacks of the hydrogen which would otherwise have energetically reduced it. At lower pressures, however, the said film became too attenuated to ensure complete protection, so that the rate of steam formation was accelerated by reason of hydrogen penetrating through on to the CuO surface and reducing it.

Precisely similar results were subsequently obtained by Bone and Andrew in experimenting upon the catalytic oxidation of carbonic oxide over nickel oxide and copper oxide surfaces, respectively, at temperatures of 150° and 165° C., respectively, so that there can be no gainsaying the facts, whatever may be their true interpretation.

Those who wish to weigh all the evidence adduced during the experiments must refer to the original papers; but the conclusion drawn from them was that, in such cases, the true catalytic combustion may be visualised as involving the formation of an active O-film, probably of more than monomolecular thickness, at the oxide surface; indeed unless such a film gets very attenuated it not only burns the combustible gas but also prevents it from penetrating to the underlying oxide surface and reducing it.

The Actions of Nickel and Copper towards Carbonic Oxide-Oxygen Mixtures

Strong evidence was obtained that the action of nickel in inducing the union of carbonic oxide-oxygen mixtures at 375° C. is largely due to the formation of a very reactive Ni-CO (or possibly O-Ni-CO) complex at the surface, although it did not exclude the possibility of its also being in part due to simultaneous 'activations' of both O_2 and CO molecules without such 'complex' formation. On the other hand, in the case of a copper gauze surface, which was very effective in inducing the catalytic combustion at 250°, the formation of Cu-CO (or O-Cu-CO) complexes was shewn to be highly detrimental to its catalysing power, which seemed to be strongest when the combining gases were merely 'occluded.' Hence it must be conceded that in special cases (*e.g.* nickel) such 'complexes' do play an important rôle.

Effects of Progressively Drying a $2CO + O_2$ *System undergoing Catalytic Combustion*

Finally, some important evidence was obtained as to the influence of steam upon the union of carbonic oxide and oxygen in contact with such hot surfaces as gold, silver, fireclay and porous porcelain, which will have to be taken into account in any general theory of catalytic combustion. It was proved, (1) that whilst the *immediate* effect of the progressive drying out of such system is always to increase the apparent catalysing power of the surface, presumably by removing from it the film of H_2O molecules which normally lags it, more or less according to the physical conditions, (2) the *ultimate* effect is to diminish greatly, or even to stop completely, the catalytic combustion. In the cases of the gold and silver surfaces at 240° and 360° C. respectively, the *ultimate* effect of a rigid 'drying' was practically to stop the combustion altogether; but on re-introducing moisture into the system its original reactivity was in time completely restored. In the case of a porcelain surface, however, whilst the *ultimate* effect of prolonged drying was to diminish greatly its catalysing power, the re-introduction of moisture into the system did not restore it. These remarkable effects are illustrated by the two curves (for $2CO + O_2$ mixtures combining over (*A*) silver at 360°, or (*B*) porous porcelain at 500° C.) shewn in Fig. 157, but the reader should consult the original paper for details of the experiments.*

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* *Proc. Roy. Soc.* A 112 (1926), pp. 474 to 499.

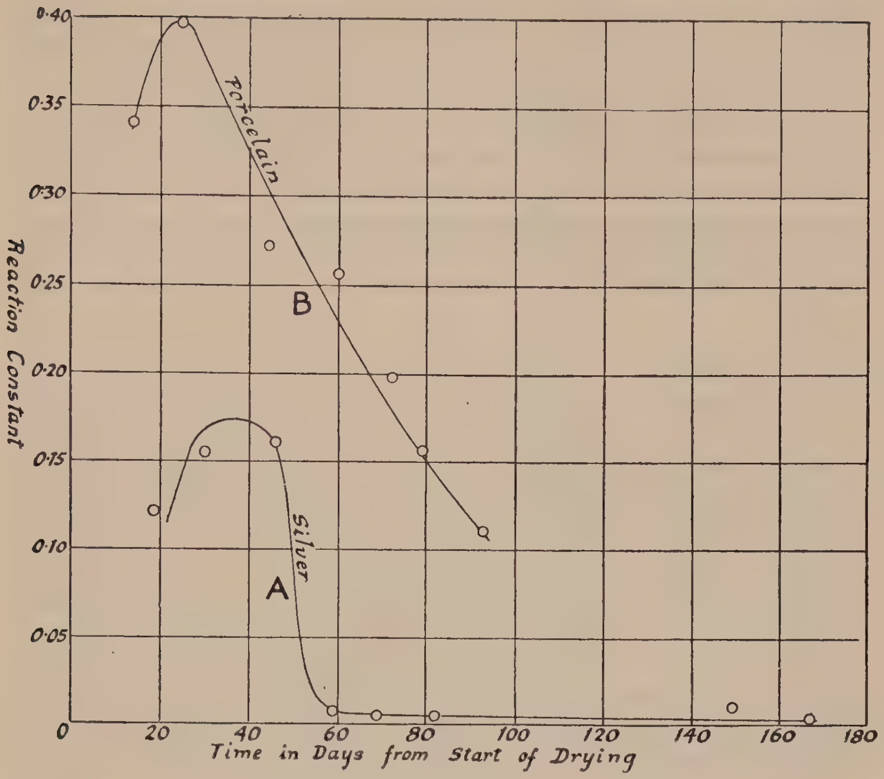

FIG. 157.

Some Theoretical Suggestions

In 1906 Bone and Wheeler had reached the conclusion that, under the conditions studied by them, the phenomenon of true surface combustion " depends primarily on a condensation of one or other (and, in some cases possibly both) of the reacting gases on the heated surface," and that the prime cause lies in an ' activation of the combining gases (certainly of the hydrogen and probably also of the oxygen) by 'association' with the surface. Also, the view was expressed that it might perhaps be attributed to the dissociation of hydrogen molecules at the moment of occlusion, and attention was directed to the extraordinary activity of hydrogen when 'condensed' by many surfaces, as well as to the observations of H. A. Wilson and Sir J. J. Thomson regarding the influence of hydrogen upon the leakage or emission of negative corpuscles from certain metals, *e.g.* from platinum at 1350°, and from alkali metals at ordinary temperatures.

In the course of a discussion upon the subject at the British Association in 1910, Sir J. J. Thomson said, " It was not improbable that the emission of charged particles from the surface was a factor of primary importance. . .

These electrons might produce very important effects by uniting (perhaps selectively) with moisture, with the oxygen, and with the inflammable constituent of the gaseous mixture. The mode of action of the oxides was specially worthy of investigation. . . . It might be that the problem of the source of energy of the torrent of electrons might be found in the oxidation and reduction of the contact substance. He suggested that the action of surfaces might ultimately be found to depend on the fact that they formed a support for layers of electrified gas in which chemical changes proceeded with high velocity." *

Langmuir's Theory

In the year 1916 Langmuir published, in his well-known memoir upon the "Constitution and Fundamental Properties of Solids and Liquids," † a theory concerning chemical actions of surfaces (heterogeneous catalytic reactions) which included and developed further the basic ideas originally put forward by Bone and Wheeler. In the course of a Discussion at the Faraday Society in 1921,‡ he acknowledged that there were a great many statements in the Bone and Wheeler memoir of 1906, "which foreshadow in a general way some of the conclusions that we have reached more recently" §; and in a subsequent private communication to one of us (W.A.B.) he admitted that "the general view-point which you had in 1906 was much ahead of others of that time, and is in many ways closely related to that which I have developed independently from a rather different experimental basis." Langmuir set out to apply to heterogeneous reactions, and to the phenomena of adsorption and surface tension, the new conception of crystal structure arising out of the work of W. H. and W. L. Bragg, and his speculative treatment of the subject has been highly suggestive and valuable. And he brought forward some new experiments on the catalytic combinations of both carbonic oxide and hydrogen with oxygen, particularly in contact with a smooth platinum surface at temperatures between 300° and 1000° K. and very low pressure (less than 0·1 mm.). He agreed with Bone and Wheeler in identifying the actions of hot surfaces in accelerating gaseous interactions with their powers of absorbing gases, although he used the term 'adsorption' where they had used 'absorption' or 'occlusion.' He further postulated that such 'adsorption' is determined by chemical affinity, and that the adsorbed layers of gas are monomolecular in thickness, in which the molecules are definitely oriented.

The following quotation from Langmuir's Faraday Society Paper will indicate the essence of his views: "When gas molecules condense on a solid surface in such a way that they are held on a surface by primary valence forces, involving a rearrangement of their electrons, their chemical properties become completely modified. It is not surprising, therefore, that in some cases such adsorbed films should be extremely reactive, while in other cases they may be very inert to outside influences. Thus oxygen adsorbed on platinum reacts readily with hydrogen or carbon monoxide, while oxygen on tungsten, or carbon monoxide on platinum, shew very little tendency to react with gases brought into contact with their surfaces. The specific nature of the behaviour of their films is quite consistent with the theory that adsorption depends on typical chemical action. In many cases, especially when we deal with adsorption of large molecules, the orientation of the molecules on the surface is a factor of vital importance in determining the activity of the surface towards reacting gases."

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* *B. A. Reports* (Sheffield), 1910, p. 501.

† *Journ. Amer. Chem. Soc.* vol. 38, pp. 2221-2295 (1916).

‡ *Trans. Faraday Soc.* xvii. (1922), pp. 545-676.

§ *Ibid.* p. 672.

In the private communication referred to Langmuir disclaimed "ever having looked upon ionization as the cause of activation in heterogeneous catalysis," saying that he had frequently made experiments to detect ionization in such cases, but without success. He thought, however, that "the electron emission may be changed by a reaction, but this is a purely secondary effect and cannot be regarded as the cause of chemical action although both electron emission and chemical action may be modified by the presence of adsorbed films."

It may here be observed that in Langmuir's experiments upon the catalytic combustion of carbon monoxide (*loc. cit.*) the conditions were very different from those of previous workers. He heated a platinum wire electrically not only to higher temperatures, which in different experiments varied from 'considerably below red heat' up to white heat, but also in mixtures of carbon monoxide and oxygen at much lower pressures (*e.g.* down to about 0·1 mm.) than those employed by previous workers.

In such circumstances he found at between 500° and 700° K. the gases reacted at a rate directly proportional to the partial pressure of the oxygen and inversely to that of the carbon monoxide; within this range the reaction velocity increased rapidly with the temperature, about 1·6 fold for 10° at 600° K. Within a range of 750° to 1050° K. the velocity was found to be independent of the temperature, being limited largely by the rate at which the gases can come into contact with the surface. At such temperatures, and with an excess of oxygen, the reaction velocity was proportional to the partial pressure of the carbon monoxide, while with an excess of the latter it was proportional to the partial pressure of the oxygen. Similar results were obtained with hydrogen-oxygen mixtures for temperature ranges 300° to 500° and 700° to 900° K., respectively, except that at the lower range they were rather erratic and dependent upon the previous treatment of the surface.

Langmuir visualised the mechanism of the reaction as follows: Every oxygen molecule which strikes a *clean* platinum surface condenses upon it in the form of single atoms combined with separate platinum atoms, such chemical union being so firm that no appreciable evaporation of O atoms from the surface takes place even when the platinum is at 1500° K. These ‘ adsorbed ’ O atoms are in a very active condition in regard to their ability to react with the CO, and *every* CO molecule which strikes such an adsorbed O atom reacts with it to form CO_2. When CO molecules strike a clean platinum surface every one condenses on it, being held by chemical union between the C atoms and two platinum atoms. An adsorbed film of CO thus consists of a monomolecular layer of oriented molecules, which, however, are not so firmly held to the surface as are O atoms, because they evaporate at an appreciable rate at temperatures as low as 500° K. And because of their said orientation the adsorbed CO molecules are chemically very inert towards oxygen. At low temperature range the surface is nearly completely covered by such an oriented adsorbed CO film, and reaction only occurs when unadsorbed CO molecules from the inter-gaseous atmosphere strike O atoms which have become adsorbed in the spaces left vacant by the evaporation of condensed CO molecules. At high temperatures the surface is nearly covered with O, so that when there is excess of it present the reaction velocity is limited by the rate at which CO molecules strike the surface; on the other hand, when excess of CO is present, the surface is largely bare, and the reaction velocity is limited by the rate at which O_2 molecules strike the surface, because the oxygen remains on the surface in an atomic condition until struck by a CO molecule.*

It is important to note that the essential points in Langmuir’s view are (1) that it is only the adsorbed oxygen which is really activated by the surface, whose function it is to atomize the O_2 molecules as they condense upon it; (2) that adsorbed CO molecules are not activated at all, but, on the contrary, are rendered chemically very inert towards oxygen, and by blanketing the surface as a monomolecular film act as a ‘ poison ’ towards it; and (3) that CO_2 is only formed when an unadsorbed CO molecule from the surrounding atmosphere strikes ‘ atomized ’ oxygen condensed on the surface.

Undoubtedly such a theory is attractive, and it has gained many adherents, but it is not free from real difficulties, in that it seems unduly to stress ‘ adsorption ’ and ‘ orientation,’ and attaches little or no importance to the influences of ‘ occluded ’ gases and of ‘ ionisation.’ And, even if true in reference to some conditions, it fails to explain the facts as a whole, and therefore cannot be regarded as comprehensive. Thus it is hard to see how it would explain the fact that complete ‘ dryness ’ entirely stops the catalytic union of carbonic oxide and oxygen over gold or silver at temperatures of 240° and 360° C. respectively. For if the catalytic combustion of carbonic oxide is conditioned merely by the formation at the surface of a unimolecular layer of the reacting gases, definitely oriented, it is not easy to see why the complete removal of water should stop it altogether. On the other hand, if the prime function of the surface is to 'ionise' the reacting gases, which in a neutral state are incapable of combining, the observed influence of water vapour in the circumstances referred to would be more understandable.

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* *Vide Trans. Faraday Society, loc. cit.* pp. 653, 654.

In this connection reference should be made to some experiments carried out some years ago at the University of Leeds by Dr. Harold Hartley upon "The Electrical Condition of a Gold Surface during the Absorption of Gases and their Catalytic Combustion," * in which it was shewn that the gold gauze surface used by Bone and his collaborators (*loc. cit.*) acquired a negative charge of approximately 0·2 volt when promoting the combination of electrolytic gas at a temperature of 350° C. as also a negative charge of between 0·7 and 0·85 volt when promoting the combination of carbon monoxide and oxygen in their combining ratios at a temperature of 370° C. Moreover, it was shewn that the metal became negatively charged in contact with either of the combustible gases, but positively charged in contact with oxygen at temperatures between 350° and 400°.

G. I. Finch and J. C. Stimson, working at the Imperial College, London, have recently repeated and extended Hartley's experiments with results of considerable significance which, however, have not yet been published. After generally confirming Hartley's observations, they extended them over a wide range of temperature up to 850° C. The results support the idea that both hydrogen and oxygen are always 'ionised' in contact with a gold surface at temperatures above 250°, which happens to be that at which it becomes really active in promoting the catalytic combustion; and the same applies also to the action of a silver surface. It would thus appear that an 'ionisation' both of the combustible gas and of the oxygen proceeds concurrently with their catalytic combustion over such surfaces.

Within the past two or three years H. S. Taylor and others have contended that as a rule only a very small fraction of the surface of a catalyst is really active, but this is a very debatable point. For although there may be now a good deal of cumulative evidence of some catalysing surfaces being sensitive to 'heat treatment' and not uniformly active all over, there is little to support what may be termed 'a leopard's skin' view of the catalyst in 'surface combustion,' however well it may be deemed by some to apply to cases of 'catalytic hydrogenation.'

Taylor has recently stated † that "for reactions in which only a relatively small fraction of the surface is catalytically active, the activity is associated with occasional groups of atoms fixed in metastable positions associated with high energy and chemical unsaturation relative to the atoms in the regular lattice of the catalyst granule. This concept, however, of the catalyst surface, satisfactory though it be, does not answer what, in the last analysis, must be the central problem of the study of contact catalysis, namely, the nature of the activation induced in the *reactants* by association with these activating centres of the surface," and he proceeded to say that recent studies in the Princeton laboratories had led to a conception of such 'activation' (in hydrogenation) being essentially a 'deformation' of the hydrogen molecules, which "may result in the production of the atomic species or it may be still more drastic and result in the production of the ions of the atoms." This, it may be observed is pretty much what Bone and Wheeler said in 1906 in respect of the action of hot surfaces in promoting the union of hydrogen and oxygen.

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* *Proc. Roy. Soc. A.* **90** (1914), pp. 61-68.

† *Proc. Roy. Soc. A.* **113** (1926), pp. 77, 78.

In the catalytic combustion of hydrogen and carbonic oxide over gold or silver, it would appear that the oxygen is 'ionised' (*i.e.* electrically charged) at the surface more rapidly than carbonic oxide. Indeed, according to the latest results of Finch and Stimson, in a *dry* system, carbonic oxide remains electrically neutral at such surfaces until a temperature of about 500° is reached, and in a 'moist' system its 'activation' at lower temperatures would seem to be conditioned by the presence of steam. Also it is perhaps not without significance that, whereas readily reducible oxides, such as those of nickel and copper, which are fairly good conductors of electricity, induce the catalytic combustion at comparatively low temperatures, a non-reducible oxide surface such as porous porcelain does not promote it until temperatures at which it begins appreciably to conduct.

Taking the evidence as a whole, it may be said that, so far as can be seen at present, the phenomena of catalytic combustion is probably dependent upon an adsorption or occlusion of the reacting gases (or at least one of them) by the surface whereby they become 'activated' by association with it, and that in some cases such 'activation' may be considered as an 'ionisation' of both the oxygen and the combustible gas. The subject requires further experimental exploration, however, before its foundations will be strong enough to bear any comprehensive theory.

CHAPTER XXXVI

INCANDESCENT SURFACE COMBUSTION

The Bonecourt Process

During 1906–7 certain observations made by W. A. Bone in extending his researches upon catalytic combustion had shewn the possibility of realising a flameless incandescent surface combustion by burning 'theoretical' gas-air mixtures in contact with surfaces of ordinary refractory materials at full red heat.

Accordingly in December, 1906, provisional arrangements were made with Messrs. Wilson and Mathiesons of Leeds, the well-known gas-fire makers, for further experiments to be tried; but, owing to circumstances connected with the appointment in 1907 by the Institution and Gas Engineers conjointly with the University of Leeds of a Committee to investigate the efficiencies of gas-fires, the project was suspended by mutual consent for a period which lasted two years.

In October, 1909, when the investigation was resumed the late C. D. M'Court became associated with it, and steps were immediately taken to attack the problem systematically at the Carlton Works of Messrs. Wilson and Mathiesons, Ltd., Leeds, where the process was proved and developed during the next three years.

On 16th October, 1909, the following statement of the problem was drawn up for future reference: "To bring a combustible mixture of gas and air in suitable proportions into contact with the interstices of an incandescent porous solid of suitable composition and porosity in such a manner as to produce a flameless, or as nearly as may be a flameless, surface or interstitial combustion whereby the porous solid shall be maintained in a continual state of incandescence." A few days later Bone and M'Court started experiments on what was afterwards described as the 'diaphragm process'; and these proving immediately successful, the first patent for it was applied for on 9th November 1909. It may be said to have realised for the first time, and in a complete form, a practicable process of 'incandescent surface combustion' using explosive gaseous mixtures and common refractory materials.

The new system of flameless 'incandescent surface combustion' which was evolved during the three following years comprised principally two processes in each of which a homogeneous explosive mixture of gas and air in proper proportions for complete combustion (or with air in slight excess thereof) was caused to burn without flame in contact with a granular incandescent solid, whereby a large proportion of the potential energy of the gas was immediately converted into radiation.*

The advantages of such a system are: (1) the combustion is greatly accelerated by the incandescent surface, and, if so desired, may be concentrated just where the heat is required; (2) the combustion is perfect with a minimum excess of air; (3) the attainment of very high temperatures is possible without the aid of elaborate 'regenerative' devices; and (4) owing to the large amount of radiant energy developed, transmission of heat from the seat of combustion to the object to be heated is very rapid.

The 'Diaphragm' or 'Radiophragm' Process

In the first process, as originally developed by Bone and M'Court in 1909, a homogeneous mixture of gas and air was allowed to flow under slight pressure through a porous diaphragm of refractory material from a suitable feeding chamber behind (see Fig. 158), and caused to burn without flame at the surface of exit, which was thereby maintained in a state of red-hot incandescence. The diaphragm was composed of granules of fire-brick bound together into a coherent block by suitable means, the porosity of the diaphragm being graded to suit the particular kind of gas used; for coal gas, or carburetted water gas, a diaphragm so porous that the gaseous mixture will readily flow through it at a pressure of $\frac{1}{8}$ inch water gauge was employed. The diaphragm was mounted in a suitable

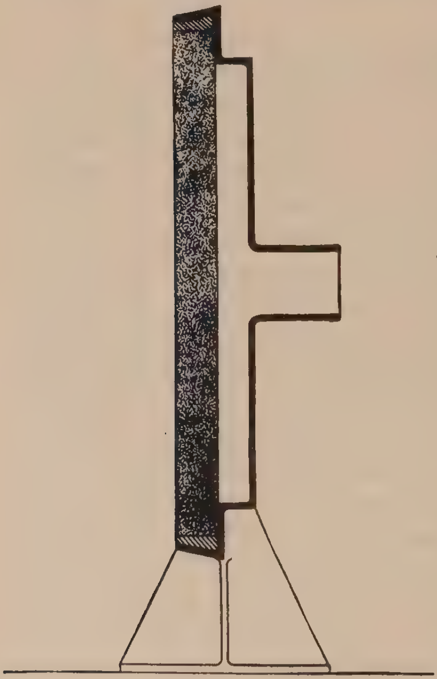

Fig. 158.

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* For a fuller account of the various developments of the subject than can be given in this chapter, the reader is referred to the following published lectures upon it by one of us, *Proc. Amer. Gas Institute*, vi. 565; *Journn. Franklin Inst.* 1912, pp. 101 to 131; *Proc. Royal Institution* (1917), pp. 41 to 62; '*Howard Lectures,*' *Royal Society of Arts in* 1914; *Ber. deut. Chem. Ges.* xlvi. (1913), p. 5; *Journ. Roy. Soc. Arts* (1923).

casing, the space enclosed between the back of the casing and the diaphragm constituting a convenient feeding chamber for the gaseous mixture which is introduced at the back.

Such a mixture may be obtained in any convenient way, *e.g.* (1) by means of suitable connections through a Y-piece with separate supplies of low pressure gas and air (2 or 3 inches w. g. only is sufficient), or (2) by means of an ‘ injector ’ arrangement connected with a supply of gas at 2 lbs. per square inch pressure, the gas in this case drawing in its own air from the atmosphere in sufficient quantity for complete combustion, and the proportions of gas and air being regulated by a simple device.

To start up such a diaphragm, gas is first of all turned on and ignited as it issues at the surface, then air is gradually added until a fully aërated mixture is obtained. In such wise the flame soon becomes non-luminous and diminishes in size ; then, a moment later, it retreats on to the surface of the diaphragm, which at once assumes a bluish appearance ; soon, however, the granules at the surface attain an incipient red heat, producing a curious mottled effect ; finally, the whole of the surface layer of granules becomes red-hot, and an accelerated ‘ surface combustion ’ comes into play. All signs of flame disappear, and there remains an intensely glowing surface—a veritable wall of fire, but without flame—throwing out a genial radiant heat, which can be steadily maintained for as long as required, the surface temperature being at about 900° to 1000° C.

In this apparatus not only was the phenomenon of flameless incandescent surface combustion for the first time effectively realised with common refractory materials, in the sense that it could always be produced easily and maintained indefinitely so long as the surface was freely radiating, but also the combustion was perfect and the ‘ radiant efficiency ’ unsurpassed. Its chief advantages are (1) the combustion is confined within a very thin layer—$\frac{1}{8}$ to $\frac{1}{4}$ inch immediately below the surface, no heat being developed in any other part of the apparatus, (2) the combustion, though confined within such narrow limits, is perfect with a minimum excess of air, no trace of unburnt gas escaping from the glowing surface, (3) a great variety of combustible gases or vapours can be employed with it (*e.g.* coal gas, natural gas, carburetted water gas, petrol-air gas, etc.), and (4) the process in no way depends upon the external atmosphere. Moreover, it was in principle very simple, and eminently adapted for a great variety of uses so long as free radiation of the surface was not greatly impeded, a circumstance which will be referred to again in describing certain improvements in the fabrication of the diaphragm made in recent years by Mr. F. J. Cox of London.*

It should be noted, that in their original patent (No. 25,808 of 1909), Bone and M‘Court described, as examples only, two methods of making the diaphragms used in the process, adding that they did not limit themselves to these, but might adopt other constructions as would enable them "to burn a mixture of gases or the like and produce within the surface of the medium a combustion with little or no flame." Also, it was stated that instead of using plane diaphragms they might employ dome-shaped or cylindrical diaphragms, or diaphragms of other special form suited to special purposes. Their principal claim was "apparatus for the burning of an explosive mixture of gases arranged so that a regulated flow of the explosive mixture through a porous diaphragm can be maintained in such wise that combustion takes place substantially within the outer surface layer of the diaphragm, which outer surface layer is thereby maintained in a state of incandescence substantially as described."

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* *Vide* paper by W. A. Bone on “ Surface Combustion ” in *Proc. Roy. Soc. Arts* (1923).

Incandescent Surface Combustion in a bed of Refractory Granular Material

The second process (which was covered by Eng. Patent, No. 29,430 of 1909) was applicable to all kinds of gaseous or vapourised fuels, and can be adapted to a great variety of both small- and large-scale industrial heating operations. It consists essentially in injecting, through a suitable orifice, at a speed greater than the velocity of back-firing, an explosive mixture of gas (or vapour) and air in their combining proportions

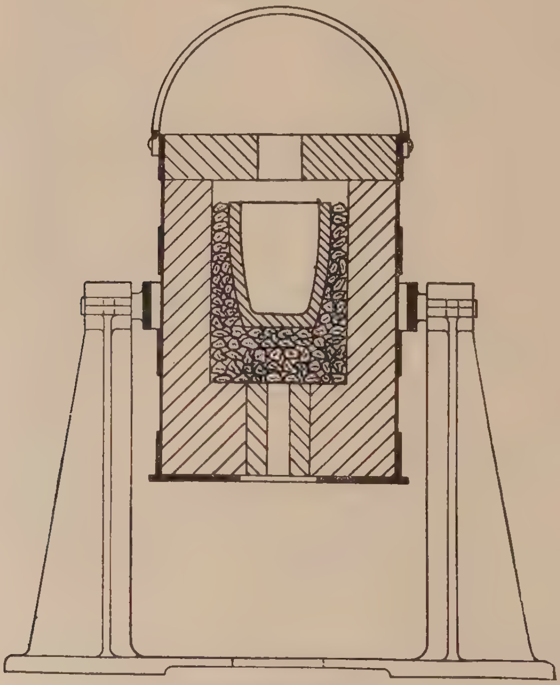

FIG. 159.

into or upon a bed of incandescent granular refractory material which is disposed around or in proximity to the body to be heated.

It may be described by the aid of two diagrams showing its applications to the heating of crucible and muffle furnaces. The first one (Fig. 159) shows the process as applied to a crucible furnace. The crucible is surrounded by a bed of highly refractory granular material. The mixture of gas and air is injected at a high velocity through a narrow orifice in the base of the furnace, and as it impinges upon the incandescent bed combustion is instantaneously completed without flame. The seat of this active surface combustion is in the lowest part of the bed; the burnt gases, rising through the upper layers, rapidly impart their heat to the bed, maintaining it in a high degree of incandescence. The next diagram (Fig. 160) shows a similar arrangement for the heating of a muffle furnace which needs no further explanation.

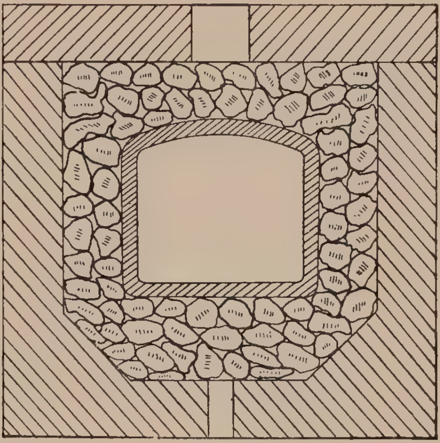

Fig. 160.

It is obvious that the process is adaptable to many other furnace operations, as, for example, to the heating of retorts, annealing furnaces, and the like. Moreover, it is not essential that the bed of refractory material shall be disposed around the vessel or chamber to be heated; it may be equally well packed into tubes or the like, traversing the substance or medium to be heated. This latter modification became important in relation to the melting of metals or alloys, and also in relation to steam raising in multi-tubular boilers. Nor does it matter how the gaseous mixture is produced and injected on or into the incandescent refractory bed, so long as substantially perfect admixture of the gases before combustion is attained.

Claims in the original patent covered apparatus for producing high temperatures by the combustion of gaseous fuel in a bed of refractory granular or like material which becomes incandescent, characterised by the following features: (i) an outer shell or body composed of refractory material and being a bad conductor of heat, (ii) an inner bed or layer composed of refractory material having interstices into which bed the combustible mixture is introduced and in which it burns, (iii) an internal chamber in which the heat is required to be utilised and which may or may not be surrounded by an internal shell of refractory material, (iv) a passage (or passages) through which the combustible mixture passes of such length and cross-section in relation to the gaseous flow that the ignition of the combustible mixture shall not travel backwards in the passage.

By this process not only is the combustion perfect with the theoretical proportion of air, but also much higher temperatures are attainable with a given gas than by the ordinary methods of flame combustion without a regenerative system; indeed, with any gas of high calorific intensity (such as coal gas, water gas, or natural gas), the upper practicable temperature limit is determined by the refractoriness of the material composing the chamber to be heated—*i.e.*, the muffle or crucible—rather than by the possibilities of the actual combustion itself.

Thus for example, in coal-gas fired crucible furnaces with special refractory linings, etc., designed by Bone and M'Court in 1910, temperatures were realised high enough to fuse Seger cone, No. 39, which according to the Reichsanstahlt in Berlin melts at 1880° C.; and during a lecture to the American Gas Institute in St. Louis on 19th October, 1911, a roll of platinum foil (mp. 1755° C.) was melted in 20 minutes (after starting cold) in a small crucible of special refractory material placed in a cylindrical furnace containing a bed of granular refractory material. "On removing and cooling the crucible, a bead of platinum somewhat larger than a full-sized grain of wheat was formed at the bottom of the crucible and exhibited to various persons in the audience." *

In estimating the temperature obtainable in such furnaces by surface combustion, regard must be had to what may be termed the relative calorific intensity of the combustible gas employed. In this connection it is of interest to compare the following combustion data for the principal gaseous fuels available for laboratory or industrial operations in the order of their relative calorific intensities.

TABLE CXXIV.—COMBUSTION DATA OF THE PRINCIPAL GASEOUS FUELS

Gas.	Per Cubic Foot of Gas Burnt.			Per 100 B.Th.Us. Net Developed on Combustion.			
	Net B.Th.Us.	Volume of Air Required.	Volume of Products.	Volume of Air Required.	Volume of Combining Mixture.	Volume of Products.	Relative Heat Capacity of Products.
Blue water gas -	290	2·29	2·82	0·79	1·14	0·97	0·95
Coal gas - -	500	4·65	5·36	0·93	1·13	1·08	1·00
Producer gas -	140	1·17	2·00	0·84	1·50	1·43	1·38
Blast furnace gas	100	0·72	1·58	0·72	1·72	1·58	1·52

Speaking generally, it should be possible with a high grade water gas or coal gas effectively to obtain temperatures up to about 2000° C. by surface combustion in a refractory granular bed without any heat recuperation. With a low grade producer gas of the above quality the maximum temperature, without heat recuperation, probably would not exceed about 1500° C. And, as regards economy, it may be said that, during competitive trials carried out in New York towards the end of 1911, it was proved that to maintain a temperature of 1400° C. in muffle furnaces of the same dimensions, those employing surface combustion consumed only half the gas required by those fired in the ordinary way by flames.

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* *Proc. Amer. Gas Inst.* vi. (1911), Part I. p. 599.

Surface Combustion as Applied to Steam-Raising

At quite an early stage in their investigations, it was realised by Bone and M'Court that their 'granular-bed process' should be applicable to steam-raising in multi-tubular boilers. Accordingly early in 1910 experiments were carried out in Leeds with such complete success that it formed a basis for a new system of gas-fired boilers (British Patent No. 4362 of 1910), which later on was developed successfully under the advice of Mr. Michael Longridge at the Skinningrove Iron Works.

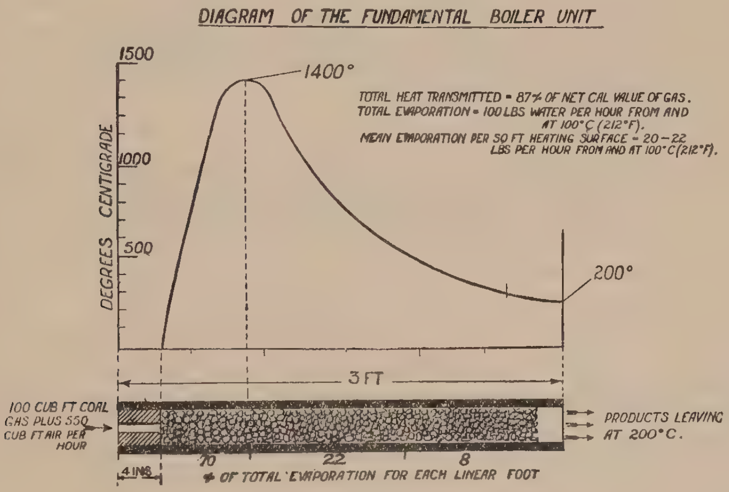
DIAGRAM OF THE FUNDAMENTAL BOILER UNIT
1500
1000
500
DEGREES CENTIGRADE
1400°
TOTAL HEAT TRANSMITTED = 87% OF NET CAL VALUE OF GAS.
TOTAL EVAPORATION = 100 LBS WATER PER HOUR FROM AND AT 100° C (212° F).
MEAN EVAPORATION PER SQ FT HEATING SURFACE = 20–22 LBS PER HOUR FROM AND AT 100° C (212° F).
200°
3 FT
100 CUB FT COAL GAS PLUS 550 CUB FT AIR PER HOUR
PRODUCTS LEAVING AT 200° C.
4 INS
70
22
8
% OF TOTAL EVAPORATION FOR EACH LINEAR FOOT

Fig. 161.

The first experiments were made with a single steel tube, 3 feet in length and 3 inches in diameter, packed with fragments of granular refractory material, meshed to a proper size, and fitted at one end with a fire-clay plug, through which was bored a circular hole $\frac{3}{4}$-inch in diameter, for the admission of the explosive mixture of gas and air at a speed greater than that of back-firing (Fig. 161). The tube was fitted into a open trough, in which water could be evaporated at atmospheric pressure.

Such a tube may be termed appropriately the fundamental unit of the boiler system, because boilers of almost any size may be constructed merely by multiplying the single tube, and as each tube is, so to speak, an independent fire or unit, the efficiency of the whole is that of the single tube, or in other words, the efficiency of the whole boiler is independent of the number of tubes fired.

Experimenting with such a tube, it was found possible to burn completely a mixture of 100 cub. ft. of coal gas plus 550 cub. feet of air per hour, and to evaporate about 100 lbs. of water from and at 100° C. (212° F.) per hour (20–22 lbs. per sq. feet of heating surface), the products leaving the further end of the tube at practically 200° C. This meant the transmission to the water of 88 per cent. of the net heat developed by the combustion, and an evaporation per sq. foot of heating surface nearly twice that of an express locomotive boiler. The combustion of the gas was completed within 4 or 5 inches of the point where it entered the tube. Of the total evaporation, no less than 70 per cent. occurred over the first linear foot of the tube, 22 per cent. over the second foot, and only 8 per cent. over the last foot. This pointed to a very effective 'radiation' transmission from the incandescent granular material in the first third of the tube, where the zone of active combustion was located, although it should be remarked that the *loci* of actual contact between the incandescent material and the walls of the tube were so rapidly cooled by the transmission of heat to the water on the other side that they never attained a temperature even approaching red heat. The granular material in the remaining two-thirds of the tube served to baffle the hot products of combustion, and to make them repeatedly impinge with high velocity against the walls of the tube, thus materially accelerating their cooling, and either preventing or minimising the formation of the feebly-conducting stationary film of relatively cold gases which in ordinary boiler practice clings to the tube walls, seriously impairing the transmission.

Although a detailed account of the subsequent developments at Skinningrove Iron Works and elsewhere would be out of place in this book, it may be recorded that two large gas-fired 'surface-combustion' boilers with 'feed-water' heaters, were installed and successfully worked there continuously for about six years (1911-1917), generating steam at 110 lbs. pressure by the combustion of washed coke-oven gas with a thermal efficiency of 92·7 per cent. on the net calorific value of the gas burnt, each boiler evaporating 5000 lbs. of water from and at 212° F. per hour. After five years' experience of them, the testimony of the management to the inventors was that, despite some difficulties connected with the corrosive action of the cooled products of combustion in the feed-water heater and fan mechanism beyond it, "the boilers themselves have proved all that you claim for them in efficiency and reliability."

In 1913 an oil-fired boiler, 5 feet in diameter and 12 feet long, containing five combustion tubes each 9 inches in diameter packed with specially designed refractory surfaces on a staggered plan, and fitted with a feed-water heater, was successfully worked in London, giving an evaporation at 125 lbs. pressure of 3000 lbs. of water per hour from and at 212° F. with a thermal efficiency of 92·5 per cent. on the *net* calorific value of the fuel consumed.

The Schnabel Process

On the 14th February, 1910, Rudolf Schnabel of Berlin was granted a patent in Germany dated from 4th September, 1908 (Nr. 218,998 Kl. 4 g. Gruppe 55), for a combustion process in which a mixture of combustible gas and air (or oxygen) was "*durch poröse Massen presst und im Innern derselben zur Verbrennung bringt.*" The process described in it involved the use of a refractory tube *A* (Fig. 162 (*a*)), filled with porous material *B*, and containing a platinum ball *D*, which was designed to work as follows: "*Leitet man durch die poröse Masse im Rohr ein Gasluftgemisch und bringt dieses beispielsweise durch eine Zündpille aus Platinschwamm zur Entzündung, dann findet die Verbrennung des Gasluftgemisches anfänglich erst in den der Zündvorrichtung zunächst liegenden Teilen der porösen Masse statt und breitet sich dann bei zunehmender Erhitzung allmählich auf die ganze Masse aus. Eine sofortige Ausdehnung des Verbrennungsprozesses auf die ganze Masse erfolgt deshalb nicht, weil die poröse Masse zu Beginn des Prozesses den verbrennenden Gasen so viel Wärme entzieht, dass eine grössere Flamme nicht bestehen kann. Der Verbrennungsprozess geht also erst dann in vollem Umfange vor sich, wenn die Masse sich, von der Zündvorrichtung ausgehend, durch das ganze Rohr hindurch gehörig erhizt hat.*"

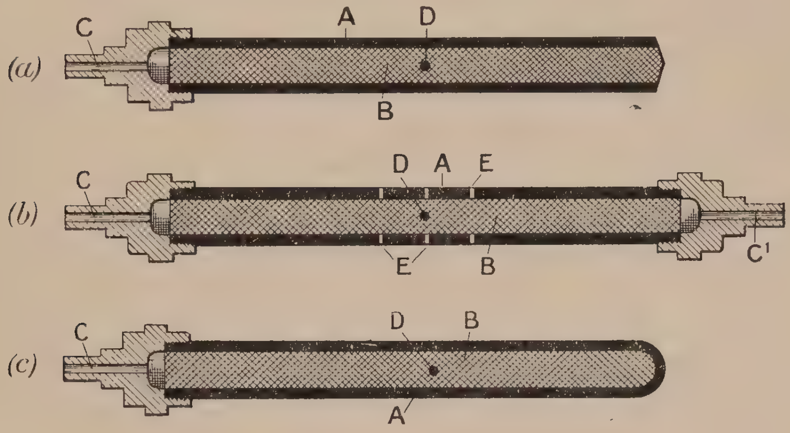

FIG. 162.

Schnabel also proposed alternative schemes in which (1) the gas and air supplies, respectively, were led in *separately* at either end of the tube, and the products of combustion allowed to flow out through a number of holes (*E*) (perforations) round the middle of the tube, as Fig. 162 (*b*), or

(2) in which the walls of the tube were made out of a gas-permeable material through which they could escape (Fig. 162 (*c*)). His principal claim was in respect of "a process for the attainment of high temperatures for heating purposes characterised in that combustible gas and air (oxygen), either separately or as a mixture, are forced through porous masses and caused to burn within them" ("*Verfahren zur Erzeugung hoher Temperaturen für Heizzwecke, dadurch gekennzeichnet, dass man brennbare Gase und Luft (Sauerstoff) getrennt oder als Gemisch durch poröse Massen presst und innerhalb derselben zur Verbrennung bringt*").

Although Schnabel here undoubtedly contemplated the use of porous masses for inducing gaseous combustion, his ideas at that time seemed to be somewhat vague about their action. It is not altogether clear whether (or how far) he had visualised an intensified surface combustion in the sense achieved by Bone and M'Court, for he believed that the gases were burnt under pressure within the porous mass of his apparatus, whereby the temperature-lowering effect of expansion was limited and the attainment of very high temperatures rendered possible. In other words he seems to have thought that combustion occurred more under '*constant-volume*' than under '*constant-pressure*' conditions. ("*. . . die Gase innerhalb der porösen Masse unter Druck zur Verbrennung kommen, wodurch die temperaturvermindernde Expansion beschränkt und die Erzeugung sehr hoher Temperaturen ermöglicht wird.*") It may also be pointed out that, apart from the practicability of the procedures described in his specification, he needed a platinum sponge to start the combustion, and in certain cases he contemplated bringing together in the combustion zone separate streams of combustible gas and air instead of introducing a mixture of them in proper proportions. Such circumstances, however, do not detract from the value of Schnabel's experiments, nor from the credit due to him as an independent investigator in the field.

Some Post-War Developments

Although the description of the manifold technical applications of incandescent surface combustion, which have followed upon the inventions already referred to, hardly pertains to this book,* a brief reference to some recent developments may not be out of place.

Before the war the applicability of incandescent surface combustion to furnaces, boilers, and other industrial apparatus had been effectively proved and demonstrated; but there remained several subordinate problems of detail, none of them very difficult but in their cumulative effect delaying, which had to be solved before any extensive industrial development could be undertaken.

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* Some of these are described in W. A. Bone's *Coal and its Scientific Uses*, Longmans Green & Co. 1918, pp. 445-476.

So far as this country was concerned, the outbreak of war in 1914 greatly impeded progress. For, soon afterwards C. D. M'Court, whose experimental skill and enthusiasm had achieved so much, relinquished surface combustion work for a Commission in the Army, hoping that in such capacity his scientific training and knowledge of men would better serve his country. Alas, he was soon numbered among those who made the supreme sacrifice, for on the 8th of October, 1916, he was killed whilst gallantly leading, as bombing officer, an attack upon the German lines. His untimely death was an irreparable loss to his colleagues as well as to the prospects of surface combustion, which he had done so much to advance.

Since the War an important advance has been made by Mr. F. J. Cox, of London, in the fabrication of the diaphragms used in the first Bonecourt process, which has overcome a certain limitation which formally handicapped their general use. The limitation referred to lay in the fact that if radiation from the diaphragms was by any means so impeded as to allow of such an accumulation of heat in the incandescent surface layer constituting the seat of the catalytic combustion as would raise its temperature much beyond 1000° C., the granular layer next below it might in time get heated up to such a degree as would render it in turn capable of promoting the catalytic combustion. The latter would then leave the surface layer and commence in the one immediately below it. It was thus possible, in circumstances of sufficiently restricted radiation, so to accumulate heat in the incandescent layers as to cause the catalytic combustion set up therein gradually to creep backwards from layer to layer in the diaphragm until pre-ignition of the combustible mixture occurred in the feeding chamber behind it. M'Court, who had himself made the very first diaphragms used, fully realised the said limitation. His diaphragms were usually made in three grades (fine, medium and coarse) to suit different combustible gases which might be employed with them, the greater the tendency of the explosive mixture to back-fire, the finer being the texture of the diaphragm employed. Before his death, M'Court had succeeded in producing diaphragms so fine grained that two of them could be placed with their incandescent surfaces opposite each other without any 'creeping back' of the combustion. Moreover, in 1913-14 an installation comprising thirteen large diaphragms made under his supervision had been employed in a factory for sugar boiling on a large scale ; one of them was used for a period of 11 months continuously, during which it had made 3000 boilings each of 20 minutes duration with a total consumption of 100,000 cub. feet of town's gas, which (it was said) was only half that required to effect the same result by means of ordinary flame-heating. The users reported such diaphragm as being "very economical in the amount of gas consumed and in every way suited for our work." It is only due to M'Court's memory that these results should be recorded, and to add that, in regard to incandescence when freely radiating, his diaphragms have not been surpassed.

These facts do not, however, detract from the importance of the improvements effected in recent years by Mr. F. J. Cox, who made a thorough study of the texture grading and manufacture generally of the diaphragms with the result that all former limitations to their use have at length been overcome. They can now be produced in quantity by his new method of manufacture of such a uniform texture and graduation of granules that no back-firing ever occurs, however much the radiation from the incandescent surface may be impeded. This development has opened up new possibilities for the old ‘ diaphragm ’ process and its success in large scale heating operations now seems assured.

In regard to other modes of applying incandescent surface combustion, it is reported that great progress has been made in the United States, where new ideas are much more favourably received and vigorously developed than here. A correspondent now in the United States writes, “ They have certainly made a wonderful thing out of it here, and it is being extensively used. They brought it into use with new mechanical devices for all manner of operations, and it is revolutionising some of the re-heating processes in metallurgy.” And, even as regards this country, where the inertia and conservatism of influential people with ‘ the NO-complex,’ constitute such a formidable obstacle to progress, it has been recently reported that “ at the present time all London newspapers are employing the surface combustion system ” for rapidly melting their type metal, and that “ in some cases the quantity of metal melted over a period of 4 to 5 hours amounts to over 400 lbs. per minute per furnace.” * In this connection it may be recalled that in 1911 Bone and M‘Court had shewn how, by surface combustion methods, 1176 lbs. of lead, charged cold at 15° C., could be melted and tapped at 372° C. per 100 cub. ft. of Leeds coal-gas (*net* cal. value=559 B.Th.U.’s per cub. ft.) consumed, which represented a thermodynamic efficiency of about 80 per cent.

Finally, as regards steam-raising in boilers, it may be doubted whether such concentration and intensive steam-raising and high efficiency as was obtained at Skinningrove Works with large multitubular gas-fired boilers only 4 feet long are possible on any other than surface combustion lines ; and if only the owners of large coke-oven plants with clean surplus gas would be enterprising enough to adopt the principle, great economies might be realised. Indeed, it may be said without exaggeration that, wherever it can be conveniently applied, ‘ incandescent surface combustion ’ is the most perfect and economical way of burning gases and vapour yet devised.

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EPILOGUE

Two hundred years ago it was believed that combustion is due to the escape of a subtle and imponderable *phlogiston* from the burning material. A century later, it was universally regarded as the result of chemical interactions between oxygen and the combustible. Nearly fifty years ago it was discovered that, in certain cases, the rigid drying of such a system renders it comparatively (if not absolutely) unreactive, and therefore that combustion is either conditioned, or greatly helped, by the presence of moisture. To-day a new vantage point has been reached from which it seems probable that in the near future we shall be able to say that combustion is conditioned by an 'ionisation' of the reacting gases.

APPENDIX

CLASSIFIED EXPERIMENTAL DATA RELATING TO IGNITION, FLAME PROPAGATION AND DETONATION

The Tables in this Appendix are adapted from those drawn up in 1926 by the Authors for the *International Critical Tables*, and are reproduced here by permission of the International Research Council.

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The data are accompanied by literature references, *e.g.* (57). At the end of each section is given a complete bibliography indexed correspondingly. A key to the periodicals, etc., is placed at the end of the Appendix.

E.g. (1) Davy, *2*, **106** : 7 ; 16. *i.e.* Davy, *Philosophical Transactions of the Royal Society*, volume 106, page 7, 1816.

1. IGNITION TEMPERATURES

Experimental Methods

A. Mixture passed through tube held at known temperature.

B. Mixture rapidly admitted to hot bulb at known temperature. Pre-flame " lag " sometimes determined by this method.

C. Bulb containing mixture heated rapidly to definite temperature.

D. Mixture passed through small reservoir while temperature was raised until flame at exit tube ran back into it.

E. Constituent gases heated separately in concentric tubes, gas from inner tube being then passed into gas in outer tube. In most recent investigations pre-flame " lag " has been controlled.

F. Constituent gases heated separately and mixed in open away from surface contact.

G. Mixture adiabatically compressed and temperature calculated from final volume.

H. Mixture adiabatically compressed and temperature calculation based on final pressure experimentally determined. Correct temperature probably lies between the values calculated by methods *G* and *H*.

I. Glass vessel within an iron one, each containing a constituent gas. Glass vessel broken at definite temperature.

J. Small drop of inflammable liquid dropped into air or oxygen maintained at a known temperature.

K. Soap bubble blown with mixture touched by hot wire at known temperature.

Pressure = 1 atm. unless otherwise noted.

H_2 HYDROGEN

Method *A* (41) Cf. (7, 9, 10, 16, 17).		Method *B*.		
		(4)		(24).
t° C*	$2H_2+O_2+$	t° C.	$2H_2+O_2+$	
605	—	550	—	For 15 % H_2 in air, 590° in 375 cm³. vessel and 625° in 9 cm³. vessel. For 60 % H_2 in air, 620° in 375 cm³. vessel and 712° in 9 cm³. vessel.
605	H_2	552–559	H_2	
611	$4H_2$			
617	$7H_2$	560–570	$3H_2$	
604	O_2	530–532	$1\frac{1}{2}O_2$	
599	$2\frac{1}{2}O_2$			
594	$4O_2$	552–553	$4N_2$	
589	$4\frac{1}{2}O_2$	560–595	$\frac{1}{2}CO_2$	
584	$7O_2$	562–592	$3CO_2$	

* All at $P=300$ mm.

Method *C* (18); Cf. (6, 9).		Method *D* (13).	Method *F* (42).
t° C.	$2H_2+O_2+$		
589	—	650° C. $2H_2+O_2$	642° C. $2H_2+O_2$
560	N_2		
543	$2N_2$		
577	$3N_2$		
609	$4N_2$		

INFLUENCE OF PRESSURE ON IGNITION TEMPERATURE (°C.) OF (*a*) H_2 IN AIR

Method *E* (50, 51, 56). Cf. (21, 43). L = lag in sec.; P in mm.

L \ P	75	100	200	400	600	750	1000	1520	2280	3800	5320
0·5	502	515	553	594	620	630	632	628	624	618	611
1	—	—	—	592	614	620	623	619	616	612	607
2	—	—	549	581	601	606	609	608	606	604	601
3	—	—	545	576	592	595	600	599	598	597	596
5	—	—	541	572	585	588	592	591	591	590	589
15	—	—	—	563	570	572	573	572	567	565	563
			(*b*) H_2 IN OXYGEN.								
0·5	500	512	550	591	—	625	—	—	618	—	—
1	—	510	547	585	—	618	—	—	610	—	—
2	—	508	544	575	—	606	—	—	595	—	—
3	—	—	541	569	—	596	—	—	580	—	—
5	—	—	539	566	—	588	—	—	565	—	—
7	—	—	538	563	—	582	—	—	555	—	—
10	—	—	536	561	—	575	—	—	546	—	—

Influence of Pressure on Ignition Temperature of H_2 in Nitrous Oxide

Method *E* (57). *L* = lag in sec. ; *P* in mm.

L \ *P*	150	250	400	550	760	1000
0·1	504	524	549	572	597	594
1	497	518	540	562	588	588
2	491	513	534	554	577	—
3	487	509	530	548	571	—
5	484	505	526	543	562	—

Method *E* (22) ; H_2 in air 470° C.

Method *G* (50, 51, 56) Cf. (20, 26, 28).		Method *H* (37).		Method *I* (36).	
t° C.*	$2H_2 + O_2 +$	*t*° C.	$2H_2 + O_2 +$	*t*° C.	$2H_2 + O_2$
521	—	410†	*ca.* $4N_2$	412	H_2
544	H_2	For 53 % H_2 in air, 460°†		433	$2H_2$
581	$2H_2$			397·5	$\frac{1}{3}O_2$
501	O_2			407	O_2
481	$3O_2$			Method *K* (31, 33)	
459	$7O_2$				
439	$15O_2$				
540	*ca.* $4N_2$				
468	*ca.* $3O_2 +$ $16N_2$				

$H_2 + Cl_2$

For $Cl_2 + H_2$ by Method *A* (9), 430°–440° ; Method *C* (9), 240°–270° ; in dark, 190° (11).

H_2S Hydrogen Sulphide

For $2H_2S + 3O_2$ by Method *A* (9), 315°–320° ; Method *C* (9), 250°–270°. For H_2S, by Method *E* (21), in O_2, 220°–235° ; in air, 346°–379°.

NH_3 Ammonia

By Method *E* (21), in O_2, 700°–860° ; (22), in air, 780°.

CO Carbonic Oxide

Method *B* (4) $M = 2CO + O_2$.

t° C.	M +	*t*° C.	M +
645–650	CO	650–657	$4N_2$
630–650	4CO	695–715	$3CO_2$
650–680	O_2		

For Method *A* and *C*, Cf. (9) ; for Method *D* (13) ; for Method *G* (19) ; Method *K* (31).

Method *E* (43) ; Cf. (21).
For CO in O_2, 665° with ½ sec. lag ; 624° with 10 sec. lag.
For CO in air, 725° with ½ sec. lag ; 685° with 10 sec. lag.
Method *B* (24) 20–70 % in air, 610°.

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* Calc. using $\gamma = 1{\cdot}4$.

† Calc. using $\gamma = 1{\cdot}32$ to allow for cooling losses during compression.

CH_4 METHANE

CH_4+2O_2, by Method *A* (9), 650°–730°; by Method *C* (9), 606°–650°. By Method *D* (13), 656°–678°.

By Method *B* (4), CH_4+2O_2 at 600°–650°; $5CH_4+2O_2$ at 640°–660°; 10 % CH_4 by vol. in air at 730°–790°. (First observation of lags prior to explosion.) Method *B* * (23, 24, 40). % = % CH_4 in air; V_{15} = temp. in 15 cm³. vessel, V_{275} in 275 cm³. vessel and V_{81} in 81 cm³. vessel.

%	V_{15}	V_{275}	%	V_{15}	V_{275}	%	V_{81}	%	V_{81}
3	737	680	10	750	710	2	711	8·8	707
6·5	736	675	12	765	710	3	700	10	714
8·0	735	680	16	807	750	5·9	695	11	724
						7·0	697	14	742

IGNITION-POINTS OF METHANE UNDER DIFFERENT PRESSURES

Method *E* (50, 51, 56). (Cf. 21, 43). For CH_4 (*a*) in air, (*b*) in oxygen. *P* = mm. pressure; *L* = lag in sec.

(*a*) IN AIR °C.

L \ *P*	100	200	400	600	760	1520	2280	3800	5320
0·6	815	788	765	753	746	722	705	675	653
1	804	768	747	737	728	711	695	666	644
2	782	733	717	712	710	690	680	652	633
3	—	715	702	696	694	676	667	640	624
5	—	697	683	679	677	666	—	—	—
7	—	685	673	668	666	—	—	—	—
10	—	673	664	659	657	—	—	—	—

(*b*) IN OXYGEN.

L \ *P*	100	200	400	600	760
0·5	728	732	720	696	670
0·6	716	721	715	688	666
1	695	697	692	675	657
2	665	660	652	645	641
3	651	643	636	631	629
5	642	633	625	621	619
7	637	626	617	612	610
10	633	621	611	604	602

Method *G* (56) CH_4+3O_2, 340° C.; CH_4+5O_2, 345° C.; CH_4+15O_2, 377° C.; 7½ % CH_4 in air, 428° C.

C_2H_2 ACETYLENE

By Method *E* (21), in O_2, 400°–440°; in air, 406°–440°. By Method *B* (24), for 45–55 % C_2H_2 in air, 335°; 20 % in air, 400°; 10 % in air, 500°.

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* The explosion occurs after certain definite time lags.

C_2H_4 ETHYLENE

For $C_2H_4+3O_2$, Method *C* (⁹), 530°–606°. By Method *B* (²⁴), for 4·5–6·5 % C_2H_4 in air (vol. vessel = 275 cm³.), 487°. By Method *E* (²¹), for C_2H_4 in O_2, 500°–519°; in air, 542°–547°. Cf. (⁹), Method *A*; (¹³), Method *D*; (³¹), Method *K*.

INFLUENCE OF PRESSURE ON IGNITION TEMPERATURE OF C_2H_4, (*a*) IN OXYGEN, (*b*) IN NITROUS OXIDE.

Method *E* (⁵⁷), *L* = lag in sec.; *P* in mm.

L \ *P*	100		150		250		400		550		760	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
0·5	594	570	617	578	650	592	660	605	624	605	604	592
1·0	581	—	600	560	634	572	646	584	613	584	593	572
2·0	563	—	580	—	614	—	625	548	601	554	584	529

C_3H_6 PROPYLENE

INFLUENCE OF PRESSURE ON IGNITION TEMPERATURE OF C_3H_6, (*a*) IN OXYGEN, (*b*) IN NITROUS OXIDE.

Method *E* (⁵⁷), *L* = lag. in sec.; *P* in mm.

L \ *P*	150		250		400		550		760	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
0·5	608	587	620	591	623	589	605	580	586	564
1·0	595	575	605	579	608	575	594	569	574	554

C_2H_6 ETHANE

By Method *B* (⁴⁷). % = % C_2H_6 in air (vol. vessel = 84 cm³.).

%	1·9	2·3	4·05	4·85	5·7	8·15	10·60
t° C.	594	571	560	555	550	540	534

For C_2H_6, Method *A*, Cf. (⁹); Method *D* (¹³). By Method *C* (⁹), for C_2H_6 + 3·5 O_2, 530°–606°. By Method *B* (²⁴), for 4–8 % C_2H_6 in air (275 cm³. vessel), 560°.

C_3H_8 PROPANE

By Method *D* (¹³), in O_2, 545°–548°. By Method *E* (²¹), in O_2, 490°–570°.

Method *B* (⁴⁷), vol. of vessel = 85 cm³.

% C_3H_8 in air -	1·25	2·50	3·05	4·90	6·50	7·85
t° C. - - - -	588	552	544	525	516	514

C_4H_{10} *n*-BUTANE

Method *B* (47), vol. of vessel = 85 cm³.

% *n*-C_4H_{10} in air -	1·25	2·00	2·60	3·65	4·85	7·65
t° C. - - -	569	545	531	515	502	489

C_4H_{10} ISOBUTANE

For *iso*-C_4H_{10} by Method *D* (13), in O_2, 545°–550°.

C_5H_{12} *n*-PENTANE

For 2–3 % C_5H_{12} in air, 512° by Method *B* (24). For 6·7 % in air, 320°–336° by Method *H* (37). Method *B* (47), vol. of vessel = 85 cm³.

% C_5H_{12} in air -	1·5	2·15	2·75	3·75	5·30	7·65
t° C. - - -	548	532	520	502	486	476

Method *E* (35a), in O_2, 550°; in air 560°–570°. Method *G* (35a), mixture composition by volume.

Pentane.	O_2	N_2	Ignition Temperature.
1	8	0	445°
1	12	0	455°
1	16	0	460°
1	24	0	460°
1	32	0	465°
1	40	0	470°
1	8	8	505°
1	8	16	510°
1	8	24	505°
1	8	32	510°

C_6H_6 BENZENE

Method -	*B.*	*J.*				*K.*
Lit. - -	(24)	(30)	(38)	(22)	(45)	(31, 33)
	In air	In O_2	In O_2	In air	In air	
	5 %, 587°	566°	570°	520°	490°	

C_6H_{14} *n*-HEXANE

By Method *G* (35a), for 2·1 % in air, 500° C. By Method *H* (37), for 6·7 % in air, 300°–306°.

C_7H_{16} *n*-HEPTANE

By Method *H* (37), for 6·7 % in air, 285° ; (39) 5 % in air, 280°.

C_8H_{18} *n*-OCTANE

By Method *H*, for 6·7 % in air, 275° (37) ; 280° (39).

PETROLEUM

Method -	*B.*	*J.*				*K.*
Lit. - -	(24)	(30)			(27)	(31, 33)
	In air		In O_2	In air	In air	
	2·2 %	Texas	256°	387°	Borneo	
	481°	Borneo	269°	380°	400°	
		Mexico	274°	424°		

C_2H_6O ETHYL ALCOHOL

Method	*B* (in air).			*E.*	*J.*			
Lit. -	(24)	(34)		(35a)	(30)	(38)	(45)	(22)
	27–28 % 450°	2%, 515–520° 3%, 505°	4%, 455–500° 5%, 480–495°	510–15† 595–600*	395°† 518°*	355°†	360°†	510*

Method *G* (35a)—Mixture Composition by Volume.

C_2H_5OH	O_2	N_2	Ignition Temperature.
1	2	—	405°
1	3	—	375°
1	5	—	380°
1	10	—	410°
1	15	—	445°
1	3	2	435°
1	3	7	515°
1	3	12	550°

$C_4H_{10}O$ ETHER

In air by Method *A* (32), 190° ; Method *B* (35), 185°–193° ; Method *J* (30), 347° ; (22), 400°. In O_2 by Method *J* (30), 190°.

By Method *B* ‡ (34), for 4·8 % in air, 178°–184° ; for 4·1 %, 179°–185° ; for 3·5 %, 180·5°–188°. By Method *E* (35a), in O_2, 235°–240° ; in air, 560°–580°. By Method *H* (39), for 6·6 % in air, 212°. Method *K*, Cf. (31, 33).

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* In air. † In O_2.

‡ Giving sub-ignition temp. with incomplete combustion.

Method *G* (35a)—Mixture Composition by Volume.

$(C_2H_5)_2O$.	O_2	N_2	Ignition Temperature.
1	6	—	315°
1	10	—	320°
1	15	—	325°
1	21	—	325°
1	30	4	325°
1	6	9	315°
1	6	15	315°
1	6	20	320°
1	6	24	320°

CS_2 CARBON DISULPHIDE

Method *E* (48).—(cf. 60).

Lag in sec. -	0·5	1	2	3	5	7	10
In O_2, ° C. -	132°	128°	123°	118°	114°	110°	107°
In air, ° C. -	156°	151°	145°	138°	130°	124°	120°

By Method *B* (5), for $CS_2 + 10O_2$ at $P = 750$ mm., 160° with 1–2 sec. lag. At $P = 300$ mm. and with 15 sec. lag, for $CS_2 + 5O_2 + 5N_2$, 155°; for $CS_2 + \frac{1}{2}O_2 + 8N_2$, 290°. By Method *F* (42), in O_2, 236°. By Method *H* (39), for 12·5 % in air, 253°.

C_2N_2 CYANOGEN

By Method *E* (21), in O_2, 803°–818°.

MISCELLANEOUS

(*a*) = acetone, (*b*) = paraffin, (*c*) = turpentine, (*d*) = creosote oil, (*e*) = palm oil, (*f*) = aldehyde, (*g*) = aniline, (*h*) = toluene, (*i*) = xylene, (*j*) = methyl alcohol, (*k*) = amyl alcohol, (*l*) = anthracene, (*m*) = naphthalene.

	(*a*)		(*b*)		(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
Method -	*B*,* ‡	*J**	*J*†	*J**	*J*	*J**	*J**	*J**	*J**
Lit. -	(34)	(22)	(30)	(22)	(30, 45)	(27)	(27)	(22)	(22)
	4 %, 500° 8 %, 500°	570°	251°	370°	275°*† 240°*	550°	400°	380°	530°

	(*h*)		(*i*)	(*j*)	(*k*)	(*l*)	(*m*)
Method -	*J*†	*J**	*J**	*J*†	*J*†	*J*†	*J*†
Lit. -	(38 30)	(22)	(22)	(38)	(38)	(38)	(38)
	563° 516°	520°	500°	500°	315°	472°	500°

* In air. † In O_2. ‡ Satd. at 15°, 505°.

LITERATURE

(For a key to the periodicals, see pp. 534-535.)

(1) Davy, *2*, 106 : 7 ; 16. (2) Bunsen, *B 1*. (3) Mitscherlich, *7*, 9 : 1171 ; 76. (4) Mallard and Le Chatelier, *5*, 91 : 825 ; 80. *15*, 1 : 173 ; 82. *9*, 4 : 274 ; 83. *14*, 39 : 2 ; 83. (5) Turpin, *11*, 1890 : 776. (6) Krause and Meyer, *16*, 264 : 85 ; 91. (7) Freyer and Meyer, *7*, 25 : 622 ; 92. (8) Askenasy and Meyer, *16*, 269 : 49 ; 92. (9) Freyer and Meyer, *17*, 1 : 28 ; 93. (10) Mitscherlich, *7*, 26 : 160 ; 93. (11) Mitscherlich, *7*, 26 : 399 ; 93. (12) Meyer, *7*, 26 : 429 ; 93. (*13*) Meyer and Munch, *7*, 26 : 2421 ; 93. (14) Meyer and Raum, *7*, 28 : 2904 ; 94. (15) Gautier and Helier, *5*, 122 : 566 ; 96. (16) Helier, *6*, 10 : 521 ; 97. (17) Bodenstein, *17*, 29 : 665 ; 99. (17a) Dixon and Russell, *3*, 75 : 600 ; 99. (18) Emich, *18*, 21 : 1061 ; 00. (19) Falk, *13*, 28 : 1517 ; 06. (20) Falk, *13*, 29 : 1536 ; 07. *10*, 24 : 450 ; 07. (21) Dixon and Coward, *3*, 95 : 514 ; 09. (22) Holm, *19*, 26 : 273 ; 13. (23) Taffanel and Le Floch, *5*, 156 : 1544 ; 13. (24) Taffanel and Le Floch, *5*, 157 : 469 ; 13. (25) Dixon, Bradshaw and Campbell, *3*, 100 : 2027 ; 14. (26) Dixon and Crofts, *3*, 100 : 2036 ; 14. (27) Constam and Schläpfer, *20*, 57 : 39 ; 14. (28) Crofts, *37*, 101 : 290, 306 ; 15, (29) Cassel, *10*, 51 : 685 ; 16. (30) Moore, *21*, 36 : 109 ; 17. (31) McDavid, *3*, 103 : 1003 ; 17. (32) Alilaire, *5*, 168 : 729 ; 19. (33) White and Price, *3*, 115 : 1248 ; 19. (34) White and Price, *3*, 115 : 1462 ; 19. (35) McClelland and Gill, *22*, 16 : 109 ; 20. (35a) Dixon, *B 2* : 20. (36) Fiesel, *17*, 97 : 158 ; 21. (37) Tizard, *23*, 37 : 381 ; 21. (38) Wollers and Emcke, *Krupp's Monatsheft*, 1921. (39) Tizard and Pye, *4*, 44 : 79 ; 22. (40) Mason and Wheeler, *3*, 121 : 2079 ; 24. (41) Mitscherlich and Reuter, *24*, 121 : 53 ; 22. (42) Wartenburg and Kannenberg, *17*, 105 : 205 ; 23. (43) Dixon, *35*, 68 : 1 ; 23. (44) Tauss and Schulte, *20*, 68 : 574 ; 24. (45) Jentzsch, *20*, 68 : 1150 ; 24. (46) Ormandy, *26*, 10 : 335 ; 24. (47) Mason and Wheeler, *3*, 125 : 1869 ; 24. (48) Dixon, *27*, 44 : 305 ; 25. (49) David, *11*, 1925 ; 303. (50) Dixon, *11*, 1925 ; 303. (51) Dixon and Higgins, *25*, 69 : 19 ; 25. (52) Coward and Wheeler, *28*, No. 8 ; 25. (53) Naylor and Wheeler, *28*, No. 9 ; 25. (54) Tizard and Pye, *4* ($_7$), 1 : 1094 ; 26. (55) Pignot, *5*, 182 : 376 ; 26. (56) Dixons, Higgins and Harwood, *29*, 22 : 267 ; 26. (57) Dixon and Higgins, *25*, 71 : 1 ; 26-27. (58) Ormandy and Craven, *26*, 12 : 650 ; 26. (59) Tanaka and Najai, *24*, 2 : 221 and 284 ; 26. (60) White, *3*, 793 ; 27.

2. ELECTRICAL IGNITION

The principal data, some of which is incorporated in the curves shewn in Chapter IX, pp. 86 to 89, does not lend itself to systematic tabulation ; the following are the principal references to the literature.

LITERATURE

(For a key to the periodicals, see pp. 534-535.)

(1) Thornton, *30*, 44 I : 145 ; 12. 46 II : 112 ; 13. (2) Thornton, *31*, 94 : 348 ; 13. *32*, 120 : 295 ; 13. *33*, 70 : 62 ; 13. (3) Thomson, *78*, 14 : 11 ; 13. (4) Thornton, *33*, 71 : 1012 ; 13. (5) Thornton, *1*, 90 : 272 ; 14. (6) Thornton, *33*, 73 : 822 ; 14. (7) Thornton, *1*, 91 : 17 ; 14. (8) Thornton, *4*, 28 : 734 ; 14. (9) Hauser, *34*, 1916 ; 521. (10) Thornton, *1*, 92 : 9 ; 16. (11) Thornton, *1*, 92 : 381 ; 16. (12) Morgan,

31, 102 : 427 ; 16. (13) Morgan, *33*, 76 : 536 ; 16. *35*, 111 : 66 ; 16. (14) Thornton, *35*, 112 : 504 ; 16. (15) Sastry, *3*, 109 : 523 ; 16. (16) Wheeler, *3*, 111 : 130 ; 17. (17) Wheeler, *3*, 111 : 411 ; 17. (18) Wright, *3*, 111 : 643 ; 17. (19) Patterson and Campbell, *36*, 31 : 168 ; 19. (20) Thornton, *4*, 38 : 613 ; 19. (21) Morgan, *3*, 115 : 94 ; 19. (22) Thornton, *4*, 40 : 345 ; 20. (23) Thornton, *4*, 40 : 450 ; 20. (24) Wheeler, *3*, 117 : 903 ; 20. (25) Morgan, *4*, 41 : 462 ; 21. (26) Morgan and Wheeler, *3*, 119 : 239 ; 21. (27) Thornton, *37*, 11 : 524 ; 22. (28) Jones, Morgan and Wheeler, *4*, 43 : 359 ; 22. (29) Thornton, *11*, 1923 ; 469. (30) Morgan, *3*, 123 : 1304 ; 23. (31) Morgan, *4*, 45 : 968 ; 23. (32) Thornton, *38*, 62 : 481 ; 24. (33) Wheeler, *3*, 125 : 1858 ; 24. (34) Wheeler, *3*, 127 : 14 ; 25. (35) Morgan, *4*, 49 : 323 ; 25. (36) Thomson, *The Conduction of Electricity through Gases*, London, Cambridge Univ. Press, 1903. (37) Morgan, *Principles of Electric Spark Ignition in Internal Combustion Engines*, London, Lockwood, 1923. (38) Wheeler, *28*, No. 20 ; 26. (39) Bone and Weston, *1*, *A* 110 : 615 ; 26.

PRE-FLAME CONDITIONS

(1) Kirkby, *4*, 7 : 223 ; 04. (2) Kirkby, *4*, 13 : 289 ; 07. (3) Kirkby, *1*, *A* 85 : 151 ; 11. (4) Lind, *39*, 21 : 177 ; 12. (5) Finch and Cowen, *1*, *A* 111 : 257 ; 26. (6) Coward and Meiter, *13*, 49 : 397 ; 27.

3. LIMITS OF INFLAMMABILITY

The limits are given in volume % and apply to atmospheric conditions of temperature and pressure unless otherwise stated. The first value in the limits column is the lowest lower limit, and the second the highest higher limit of the experimentally found values, which usually agree within a few tenths of 1 %.

ABBREVIATIONS

E_v - -	Explosion in closed vessel of volume v, cm³. generally stated.
Fl_D - -	Downward propagation of flame.
Fl_H - -	Horizontal propagation of flame.
Fl_U - -	Upward propagation of flame.
Atm. - -	Nature of atmosphere.
Tb_x - -	Tube whose diameter $= x$ cm.
Sat.$_x$ - -	Gases saturated with H_2O vapour at x°.
$P_{x \text{ at}}$ - -	Pressure, x atmospheres.
$P_{x \text{ mm}}$ - -	Pressure, x mm. Hg.

All temperatures are in ° C.

H_2 Hydrogen

Atm.	Limits.	Experimental Conditions.	Literature Ref.
O_2	9·4 –91·0	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, Sat.$_{17\cdot5}$	(12)
	9·0 –93·3	100°	
Air	9·2 –65·0	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, Sat.$_{17\cdot5}$	(12)
	9·2 –68·5	100°	
Air	9·0 –62·8	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, dried by P_2O_5,	(12)
	9·0 –68·6	100°	
$CO_2 : O_2$ 79 : 21	11·7 –68·4	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, Sat.$_{17\cdot5}$	(12)
	11·4 –69·4	100°	
Air	5·0 –72·0	Glass, $\mathrm{Tb_{7\cdot5}}$, $\mathrm{Fl_U}$	(14)
Air	10·0 –	$\mathrm{E_{2000}}$	(18)
Air	9·5 –66·3		(19)
Air	9·45–66·4	$\mathrm{E_{110}}$, Sat.	(23)
Air	9·73–63·6	$\mathrm{Tb_{1\cdot4}}$, $\mathrm{Fl_D}$	(25)
O_2	5·45–94·7	Sat.$_{15-18}$	(28)
Air	8·7 –	$\mathrm{E_{100}}$, $\mathrm{Fl_D}$	(33)
O_2	8·7 –		(33)
Air	9·05–68·6 *	$P_{2-3\ \mathrm{at}}$ $\mathrm{E_{1940}}$, $\mathrm{Fl_D}$	(36)
	9·28–68·0	$P_{5-6\ \mathrm{at}}$	(36)
	9·47–67·5	$P_{10\ \mathrm{at}}$	(36)
Air	4·1 –	$\mathrm{E_{170\,000}}$, $\mathrm{Fl_U}$, Sat.$_{17-18}$	(39)
Air	4·1 –60·6		(51)
Air	10 –66·0	$\mathrm{E_V}$	(52)
Air	–74·2	Sat.$_{\mathrm{room}}$ 15 *l* vessel	(56)
Air	9·4 –65·3	$\mathrm{E_{120}}$ $\mathrm{Fl_D}$	(60)
O_2	9·1 –91·7	$\mathrm{E_{120}}$ $\mathrm{Fl_D}$	(60)
$O_2 : N_2$ 40·1 : 59·9	9·2 –81·2	$\mathrm{E_{120}}$ $\mathrm{Fl_D}$	(60)
$O_2 : N_2$ 56·2 : 43·8	9·2 –86·4	$\mathrm{E_{120}}$ $\mathrm{Fl_D}$	(60)
Air	9·46–64·5	Glass pipette	(73)
	9·42–65·9	Glass bulb	(73)
	10·78–59·8	(20°) Iron tube	(73)
	9·27–67·5	100°	
	8·98–72·2	200°	
	8·62–79·1	300°	
Air	4·15–75·0	$\mathrm{Fl_U}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	6·50–	$\mathrm{Fl_H}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	8·8 –74·5	$\mathrm{Fl_D}$, $\mathrm{Tb_{7\cdot5}}$	(74)
Air	9·40–71·5	17 ± 3° $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot5}}$	(78)
	9·2 –	50°	
	8·8 –73·5	100°	
	8·3 –	150°	
	7·9 –76·0	200°	
	7·5 –	250°	
	7·1 –79·0	300°	
	6·7 –	350°	
	6·3 –81·5	400°	

* These limits are for complete combustion.

H_2S HYDROGEN SULPHIDE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	4·5 –19·0		(51)
Air	5·9 –27·2	Fl$_{H}$, Tb$_{6}$	(72)
Air	4·30–45·5	Fl$_{U}$, Tb$_{7·5}$	(74)
	5·30–35·0	Fl$_{H}$, Tb$_{7·5}$	(74)
	5·85–21·3	Fl$_{D}$, Tb$_{7·5}$	(74)

NH_3 AMMONIA

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	16·2 –27·0	E$_{500}$, sphere	(34)
O_2	15 –80	Found by altering burner mixture	(45)
Air	16·1 –26·6	Fl$_{U}$, Tb$_{5}$, 18°	(65)
	18·2 –25·5	Fl$_{H}$, Tb$_{5}$, 18°	(65)
	22·1 –23·3	Fl$_{D}$, Tb$_{5}$, 70°	(65)
	21·0 –24·6	Fl$_{D}$, Tb$_{5}$, 90°	(65)
	15·0 –28·7	Fl$_{U}$, Tb$_{5}$, 140°	(65)
	17·0 –27·5	Fl$_{H}$, Tb$_{5}$, 140°	(65)
	19·9 –26·3	Fl$_{D}$, Tb$_{5}$, 140°	(65)
	14·0 –30·4	Fl$_{U}$, Tb$_{5}$, 250°	(65)
	15·9 –29·6	Fl$_{H}$, Tb$_{5}$, 250°	(65)
	17·8 –28·2	Fl$_{D}$, Tb$_{5}$, 250°	(65)
	13·0 –32·2	Fl$_{U}$, Tb$_{5}$, 350°	(65)
	14·7 –31·1	Fl$_{H}$, Tb$_{5}$, 350°	(65)
	16·0 –30·0	Fl$_{D}$, Tb$_{5}$, 350°	(65)
	12·3 –33·9	Fl$_{U}$, Tb$_{5}$, 450°	(65)
	13·5 –33·1	Fl$_{H}$, Tb$_{5}$, 450°	(65)
	14·4 –32·0	Fl$_{D}$, Tb$_{5}$, 450°	(65)
	17·1 –26·4	Fl$_{U}$, Tb$_{7·5}$, 18°	(65)
	17·4 –26·3	Fl$_{H}$, Tb$_{7·5}$, 18°	(65)
O_2	15·3 –79·0	Fl$_{U}$, Tb$_{5}$, 18°	(65)
	16·7 –79·0	Fl$_{H}$, Tb$_{5}$, 18°	(65)
	14·8 –	Fl$_{H}$, Tb$_{5}$, 250°	(65)
	15·8 –	Fl$_{D}$, Tb$_{5}$, 250°	(65)
	12·6 –	Fl$_{H}$, Tb$_{5}$, 450°	(65)
	13·5 –	Fl$_{D}$, Tb$_{5}$, 450°	(65)
	14·8 –	Fl$_{U}$, Th$_{7·5}$, 18°	(65)
	15·6 –	Fl$_{H}$, Tb$_{7·5}$, 18°	(65)
	17·3 –	Fl$_{D}$, Tb$_{7·5}$, 18°	(65)

CO Carbonic Oxide

Atm.	Limits.	Experimental Conditions.	Literature Ref.
O_2	15·4 –94·1	15° } Fl_H, Tb_4, Sat.$_{17\cdot5}$	(12)
	14·4 –94·8	100°	
Air	14·1 –74·8	15° } Fl_H, Tb_4, Sat.$_{17\cdot5}$	(12)
	13·0 –77·6	100°	
$CO_2 : O_2$	21·6 –73·1	15° } Fl_H, Tb_4, Sat.$_{17\cdot5}$	(12)
79 : 21	20·0 –75·1	100°	
Air	13·0 –75·0	Fl_U, $Tb_{7\cdot5}$	(14)
	15·9 –74·5	Fl_H, Tb_4	(14)
Air	19·1 –61·7	$Tb_{0\cdot6}$	(17)
	38·0 –57·0	$Tb_{0\cdot3}$*	(17)
	16·4 –	P_{400}	(17)
	18·6 –	P_{130}	(17)
	27·9 –	P_{85}	(17)
	14·2 –	400°	(17)
	9·3 –	470°	(17)
	7·4 –	575°	(17)
Air	16·0 –		(18)
Air	17·3 –74·8		(19)
Air	16·5 –75·0	E_{110}, Sat.	(23)
Air	14·5 –	100° } E_{100}, Fl_D, Sat.$_{15-18}$	(33)
O_2	15·7 –	100°	(33)
Air	15·9 –72·9 †	$P_{1\ at}$, } E_{1940}	(36)
	18·4 –62·0	$P_{10\ at}$, } Fl_D	(36)
Air	12·5 –	$E_{170\,000}$, Fl_D Sat.$_{17-18}$	(39)
Air	12·6 –70·0		(51)
Air	15·0 –73·0	Sat.$_{room}$	(52)
Air	–74·2	15 *l* vessel	(56)
Air	15·55–71·0	E_{120} Fl_D	(60)
O_2	16·63–93·6	E_{120} Fl_D	(60)
$O_2 : N_2$			
37·8 : 63·2	15·85–83·6	E_{120} Fl_D	(60)
50·8 : 49·2	15·85–87·7	E_{120} Fl_D	(60)
Air	15·75–68·9	Glass pipette	(73)
	15·4 –71·6	Glass bulb	(73)
	15·8 –63·8	(20°) } Iron tube	(73)
	14·05–69·6	100°	
	13·80–76·6	200°	
Air	12·8 –75·0	Fl_U, $Tb_{7\cdot5}$	(74)
	13·6 –	Fl_H, $Tb_{7\cdot5}$	(74)
	15·3 –70·5	Fl_D, $Tb_{7\cdot5}$	(74)
Air	16·3 –70·0	17 ± 3° } Fl_D, $Tb_{2\cdot5}$	(78)
	15·7 –	50°	
	14·8 –71·5	100°	
	14·2 –	150°	
	13·5 –73·0	200°	
	12·9 –	250°	
	12·4 –75·0	300°	
	12·0 –	350°	
	11·4 –77·5	400°	

* No mixture can propagate flame through glass Tb $< 0{\cdot}23$.

† These limits are for complete combustion.

CH_4 METHANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
O_2	6·0 –57·3	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, Sat.$_{17\cdot5}$	(12)
	5·7 –57·4	100°	
Air	5·7 –13·2	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, Sat.$_{17\cdot5}$	(12)
	5·5 –13·2	100°	
	5·8 –12·8	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, dried over P_2O_5	(12)
	5·8 –13·6	100°	
$CO_2 : O_2$ 79 : 21	8·7 –11·9	15° $\mathrm{Fl_H}$, $\mathrm{Tb_4}$, Sat.$_{17\cdot5}$	(12)
	8·5 –12·2	100°	
Air	5·0 –13·0	$\mathrm{Fl_U}$, $\mathrm{Tb_{7\cdot5}}$	(14)
	6·0 –11·0	$\mathrm{Fl_D}$, $\mathrm{Tb_{7\cdot5}}$	(14)
Air	6·0 –	$\mathrm{E_{2\,000}}$	(18)
Air	6·4 –12·8		(19)
Air	6·1 –12·8	$\mathrm{E_{110}}$, Sat.	(23)
	6·3 –	$\mathrm{Fl_D}$, $\mathrm{Tb_{6\cdot2}}$	(23)
Air	5·6 –	$\mathrm{E_V}$, sphere 16 cm. diam., central ignition	(30)
Air	6·0 –	100° $\mathrm{Fl_D}$, $\mathrm{E_{100}}$, $\mathrm{Sat_{1\cdot5-18}}$	(33)
O_2	6·25–	100°	(33)
Air	6·0 –13·0 *	$P_{1\,\mathrm{at}}$ $\mathrm{Fl_D}$, $\mathrm{E_{1940}}$	(36)
	6·6 –14·0	$P_{10\,\mathrm{at}}$	
$N_2 : O_2 : CO_2$			
81 : 19	5·5 –13·5	Limits given are for explosion in a large steel bomb	(32)
31 : 19 : 50	8·0 –11·3		
83 : 17	5·7 –11·8		
40 : 17 : 43	8·3 –8·7		
85 : 15	5·9 –9·6		
64 : 15 : 21	7·3 –7·5		
87 : 14	6·3 –7-·1		
85 : 13 : 2	6·6 –6·8		
O_2	5·99–	$\mathrm{E_V}$, sphere 16 cm. diam.	(38)
$O_2 : N_2$		$\mathrm{E_V}$, sphere 16 cm. diam.	(38)
80 : 20	5·95–		
60 : 40	5·90–		
40 : 60	5·82–		
30 : 70	5·77–		
25 : 75	5·76–		
20 : 80	5·78–		
19·81	5·84–		
13·4 : 86·6	6·41–		
13 : 87	6·63–		
Air	5·3 –	$\mathrm{E_{170\,000}}$, Sat.$_{15-18}$	(39)
Air		Ignition at :	
	5·6 –14·8	Centre $\mathrm{E_V}$, 16 cm. sphere	
	5·4 –14·8	Top	(41)
	6·0 –13·4	Bottom	(41)
	5·4 –14·3	$\mathrm{Fl_D}$, $\mathrm{E_V}$, $\mathrm{Tb_6}$	(41)
$O_2 : N_2$ 20·9 : 79·1	5·60–14·8		(42)

* These limits are for complete combustion.

CH_4 METHANE—*Continued.*

Atm.	Limits.	Experimental Conditions.	Literature Ref.
19·2 : 80·8	–12·9		
18·3 : 81·7	–11·9		
17·0 : 83·0	5·80–10·6		
15·8 : 84·2	5·83–8·96		
14·9 : 85·1	6·15–8·36		
13·9 : 86·1	6·35–7·26		
13·5 : 86·6	6·50–6·70		
13·3 : 86·8	*		
Air	5·76–	Fl_D	(43)
	5·56–	Fl_H	(43)
	5·52–	Fl_U	(43)
Air	4·9 –	Fl_U Box, 5·75 ft. cube	(47)
	5·7 –	Fl_D	
	5·5 –	Fl_H	
	5·0 –	Fl_U, E_{2800}	(47)
	–13·9	Fl_D, Tb_{30}	(47)
	–15·4	Fl_U, Tb_{30}	(47)
	5·5 –13·2	Fl_D, E_{100}	
Air	5·46–	25°, E_{100}	(48)
	4·98–	200°, E_{100}	(48)
	4·75–	300°, E_{100}	(48)
	4·55–	400°, E_{100}	(48)
	3·75–	500°, E_{100}	(48)
	5·5 –	$P_{1-5 \text{ at}}$, E_{100}	(48)
Air	5·6 –14·8		(51)
Air	5·5 –14·5		(52)
Air	6·00–13·4	20°, Fl_D, E_V	(55)
	5·45–13·5	100°, Fl_D, E_V	(55)
	5·20–13·6	150°, Fl_D, E_V	(55)
	5·05–13·9	200°, Fl_D, E_V	(55)
	4·60–14·0	250°, Fl_D, E_V	(55)
	4·40–14·3	300°, Fl_D, E_V	(55)
	4·15–	350°, Fl_D, E_V	(55)
	4·00–14·7	400°, Fl_D, E_V	(55)
	3·65–15·4	500°, Fl_D, E_V	(55)
	3·35–16·4	600°, Fl_D, E_V	(55)
	3·25–18·8	700°, Fl_D, E_V	(55)
	–23·6	750°, Fl_D, E_V	(55)
	–29·0	800°, Fl_D, E_V	(55)
Air	6·00–13·0	P_{760}, Fl_D, E_V	(55)
	6·05–13·2	P_{1250}, Fl_D, E_V	(55)
	–13·4	P_{2100}, Fl_D, E_V	(55)
	6·20–13·6	P_{2900}, Fl_D, E_V	(55)
	6·25–	P_{3350}, Fl_D, E_V	(55)
	–13·8	P_{3750}, Fl_D, E_V	(55)
	6·40–14·1	P_{4650}, Fl_D, E_V	(55)
Air	–15·4	15 *l* litre vessel $Sat._{room}$	(56)
$O_2 : N_2$ 13·7 : 86·3	6·4 –6·9	Fl_H, $Tb_{2·5}$	(58)

* No mixture capable of propagating flame.

CH_2 METHANE—*Continued.*

Atm.	Limits.	Experimental Conditions.	Literature Ref.
17·0 : 83·0 -	6·1 –8·9	Fl$_{\mathrm{H}}$, Tb$_{2\cdot5}$	(^{58})
21·0 : 79·0 - -	5·8 –13·3	Fl$_{\mathrm{H}}$, Tb$_{2\cdot5}$	
33·0 : 67·0 -	5·8 –25·1	Fl$_{\mathrm{H}}$, Tb$_{2\cdot5}$	
50·0 : 50·0 -	5·8 –38·8	Fl$_{\mathrm{H}}$, Tb$_{2\cdot5}$	
66·0 : 34·0 -	5·8 –47·5	Fl$_{\mathrm{H}}$, Tb$_{2\cdot5}$	
O_2 - - -	5·7 –59·2	Fl$_{\mathrm{H}}$, Tb$_{2\cdot5}$	(^{58})
Air - -	6·05–12·1	E_{120}, Fl$_{\mathrm{D}}$	(^{60})
O_2 - - -	6·39–52·1	E_{120}, Fl$_{\mathrm{D}}$	(^{60})
$O_2 : N_2$			(^{60})
45·2–54·8 -	6·26–29·7	E_{120}, Fl$_{\mathrm{D}}$	
62·2–37·8 -	6·30–38·6	E_{120}, Fl$_{\mathrm{D}}$	
86·3–13·8 -	6·44–47·8	E_{120}, Fl$_{\mathrm{D}}$	
Air - -	5·62–13·31	P_{760}, Fl$_{\mathrm{H}}$, Tb$_2$	(^{71})
	5·62–14·25	P_{1900}, Fl$_{\mathrm{H}}$, Tb$_2$	(^{71})
	5·62–15·02	P_{3190}, Fl$_{\mathrm{H}}$, Tb$_2$	(^{71})
	5·62–15·75	P_{4270}, Fl$_{\mathrm{H}}$, Tb$_2$	(^{71})
	5·62–16·12	P_{4900}, Fl$_{\mathrm{H}}$, Tb$_2$	(^{71})
Air - -	6·12–13·6	Glass pipette	(^{73})
	5·82–13·6	Glass bulb	(^{73})
	6·25–12·8	(20°) Iron tube	(^{73})
	6·02–13·9	100°	
	5·91–14·1	200°	
	5·80–14·1	300°	
Air - -	5·35–14·9	Fl$_{\mathrm{U}}$, Tb$_{7\cdot5}$	(^{74})
	5·40–14·0	Fl$_{\mathrm{H}}$, Tb$_{7\cdot5}$	(^{74})
	5·95–13·4	Fl$_{\mathrm{D}}$, Tb$_{7\cdot5}$	(^{74})
Air - -	6·30–12·9	$17 \mp 3°$ Fl$_{\mathrm{D}}$, Tb$_{2\cdot5}$	(^{78})
	6·20–	50°	
	5·95–13·7	100°	
	5·75–14·1	150°	
	5·5 –14·6	200°	
	5·30–	250°	
	5·10–15·5	300°	
	4·95–	350°	
	4·80–16·6	400°	
	4·55–	450°	
Air - -	5·4 –14·1	E_V, Tb$_{1\cdot5}$	(^{75})

C_2H_2 ACETYLENE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air		Fl_H, $Tb_{0\cdot05}$	(13)
	7·7 –10·0	Fl_H, $Tb_{0\cdot08}$	(13)
	5·0 –15·0	Fl_H, $Tb_{0\cdot2}$	(13)
	4·5 –25·0	Fl_H, $Tb_{0\cdot4}$	(13)
	4·0 –40·0	Fl_H, $Tb_{0\cdot6}$	(13)
	3·5 –55·0	Fl_H, $Tb_{2\cdot0}$	(13)
	3·1 –62·0	Fl_H, $Tb_{3\cdot0}$	(13)
	2·9 –64·0	Fl_H, $Tb_{4\cdot0}$	(13)
Air	2·8 –65·0	Continuous propagation, in large vol.	(18)
O_2	2·8 –93·0		
Air	3·8 –40·0		(19)
Air	3·0 –82·0	Fl_D, $Tb_{7\cdot5}$	(14)
Air	3·35–52·3	E_{110}, Sat.	(23)
Air	1·53–58·7	Fl_D, $Tb_{1\cdot4}$	(25)
Air	2·82–51·7	Fl_D, E_{100}	(46)
	–73·0	Fl_U, $E_{2\ 800}$	(46)
	2·98–	Fl_{U-D}, E_{2800}	(46)
	2·53–	Fl_U, $E_{28\ 317}$	(46)
	2·87–	Fl_D, $E_{28\ 317}$	(46)
Air	3·0 –46·0		(51)
Air	3·0 –73·0		(52)
Air	3·4 –52·5	E_{120}	(60)
O_2	3·4 –90·0	E_{120}	(60)
$O_2 : N_2$			(60)
40·5 : 59·5	3·4 –74·4	E_{120}	
58·0 : 42·0	3·4 –82·4	E_{120}	
78·5 : 21·5	3·4 –87·4	E_{120}	
Air	2·68–	Glass pipette	(73)
	2·39– upper limit indefinite.	Glass bulb	(73)
	3·12–	(20°) Iron tube	(73)
	1·95–	100°	
	1·95–	200°	
Air	2·60–80·5	Fl_U, $Tb_{7\cdot5}$	(74)
	2·68–78·5	Fl_H, $Tb_{7\cdot5}$	(74)
	2·78–71·0	Fl_D, $Tb_{7\cdot5}$	(74)
Air	2·90–55·0	17 ± 3° Fl_D, $Tb_{2\cdot5}$	(78)
	2·83–59·0	50°	
	2·68–65·0	100°	
	2·52–73·0	150°	
	2·39–81·0	200°	
	2·30–	250°	
	2·19–	300°	

C_2H_4 ETHYLENE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	4·0 –22·0	Fl_U, $Tb_{7\cdot5}$	(14)
Air - -	4·1 –14·6	E_{110}, Sat.	(23)
	3·4 –	Fl_D, $Tb_{6\cdot2}$, Sat.	(23)
Air - -	5·7 –17·5		(51)
Air - -	3·8 –14·2	E_{120}, Fl_D	(60)
O_2 - - -	4·0 –62·0	E_{120}, Fl_D	(60)
$O_2 : N_2$			(60)
40·4 : 59·6 -	4·0 –47·7	E_{120}, Fl_D	
74·7 : 25·3 -	4·0 –56·4	E_{120}, Fl_D	
Air - -	3·4 –14·1	Fl_H, $Tb_{2\cdot5}$	(62)
	3·6 –13·7	Fl_D, $Tb_{2\cdot5}$	(62)
	3·2 –25·6	Fl_U, $Tb_{2\cdot5}$	(62)
Air - -	3·52–	Glass pipette	(73)
	3·34–	Glass bulb	(73)
	3·69–	(20°) Iron tube	(73)
	3·22–	100°	
	3·40–	200°	
Air - -	3·02–34·0	Fl_U, $Tb_{7\cdot5}$	(74)
	3·20–23·7	Fl_H, $Tb_{7\cdot5}$	(74)
	3·33–15·5	Fl_D, $Tb_{7\cdot5}$	(74)
Air - -	3·45–13·7	17 ± 3°	
	3·35–	50° Fl_D, $Tb_{2\cdot5}$	(78)
	3·20–14·1	100°	
	3·10–	150°	
	2·95–14·9	200°	
	2·85–15·7	250°	
	2·75–17·9	300°	
	2·60–	350°	
	2·50–	400°	

C_2H_6 ETHANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	3·10–	Centre ignit. E_V, sphere 16 cm. diam.	(30)
Air - -	3·10–10·7		(51)
Air - -	2·5 –5·0		(52)
Air - -	3·3 –10·6	Fl_H	(58)
Air - -	3·9 –9·6	E_{120}, Fl_D	(60)
O_2 - - -	3·9 –46·2	E_{120}, Fl_D	(60)
$O_2 : N_2$			(60)
37·4 : 63·6 -	3·80–21·9	E_{120}, Fl_D	
59·6 : 40·5 -	3·90–33·6	E_{120}, Fl_D	
74·7 : 25·3 -	3·80–39·7	E_{120}, Fl_D	
Air - -	3·13–9·85	P_{760}, Fl_D, $Tb_{2\cdot0}$	(71)
	–10·05	P_{1220}, Fl_D, $Tb_{2\cdot0}$	(71)
	3·13–	P_{1700}, Fl_D, $Tb_{2\cdot0}$	(71)
	–10·25	P_{1850}, Fl_D, $Tb_{2\cdot0}$	(71)

C_2H_6 ETHANE—*Continued*

Atm.	Limits.	Experimental Conditions.	Literature Ref.
	3·15–	P_{2150}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	–10·45	P_{2360}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	–10·80	P_{3190}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	3·19–	P_{3440}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	3·22–	P_{4260}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	–11·16	P_{4740}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
Air - -	3·12–15·0	$\mathrm{Fl_U}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	3·15–12·9	$\mathrm{Fl_H}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	3·26–10·2	$\mathrm{Fl_D}$, $\mathrm{Tb_{7\cdot5}}$	(74)

C_3H_6 PROPYLENE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	2·18–9·7	$\mathrm{Fl_U}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	2·22–9·3	$\mathrm{Fl_H}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	2·26–7·4	$\mathrm{Fl_D}$, $\mathrm{Tb_{7\cdot5}}$	(74)

C_3H_8 PROPANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	2·15–	Centre ignit. $\mathrm{E_V}$, sphere 16 cm. diam.	(30)
Air - -	2·17–7·35		(51)
Air - -	2·4 –7·3	$\mathrm{Fl_H}$, $\mathrm{Tb_{2\cdot5}}$	(58)
Air - -	2·40–6·69	P_{760}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	2·36–	P_{940}, Fl,$_{\mathrm{D}}$ $\mathrm{Tb_{2\cdot0}}$	(71)
	–6·88	P_{1320}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	–7·03	P_{2300}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	2·36–	P_{2620}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	–7·12	P_{2670}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	2·40–	P_{3400}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	–7·35	P_{3760}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	2·44–	P_{4270}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)
	–7·49	P_{4740}, $\mathrm{Fl_D}$, $\mathrm{Tb_{2\cdot0}}$	(71)

C_4H_8 BUTYLENE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	1·70–9·0	$\mathrm{Fl_U}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	1·75–9·0	$\mathrm{Fl_H}$, $\mathrm{Tb_{7\cdot5}}$	(74)
	1·80–6·3	$\mathrm{Fl_D}$, $\mathrm{Tb_{7\cdot5}}$	(74)

C_4H_{10} *n*-BUTANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·60–	Centre ignit. E_V, sphere 16 cm. diam.	(30)
Air	1·55–5·7		(51)
Air	1·9 –6·5	Fl_H, $Tb_{2\cdot5}$	(58)
Air	1·92–5·50	P_{760}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·89–	P_{970}, Fl_D, $Tb_{2\cdot0}$	(71)
	–5·54	P_{1120}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·86–	P_{1430}, Fl_D, $Tb_{2\cdot0}$	(71)
	–5·65	P_{1790}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·86–	P_{2460}, Fl_D, $Tb_{2\cdot0}$	(71)
	–5·75	P_{2570}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·89–	P_{3450}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·92–	P_{4330}, Fl_D, $Tb_{2\cdot0}$	(71)
	–6·00	P_{4380}, Fl_D, $Tb_{2\cdot0}$	(71)

C_5H_{12} *n*-PENTANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·1 –		(18)
Air	1·35–	E_V, sphere 16 cm. diam.	(30)
Air	2·4 –4·9	E_{110}, Sat.	(23)
Air	1·35–4·5		(51)
Air	1·6 –5·4	Fl_H, $Tb_{2\cdot5}$	(58)
Air	1·75–4·68	P_{760}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·68–	P_{1280}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·61–	P_{1640}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·59–4·91	P_{1790}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·59–	P_{2050}, Fl_D, $Tb_{2\cdot0}$	(71)
	–5·12	P_{2780}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·61–5·32	P_{3760}, Fl_D, $Tb_{2\cdot0}$	(71)
	–5·42	P_{4220}, Fl_D, $Tb_{2\cdot0}$	(71)
	1·68–	P_{4280}, Fl_D, $Tb_{2\cdot0}$	(71)
Air	1·42–8·0	Fl_U, $Tb_{7\cdot5}$	(74)
	1·44–7·45	Fl_H, $Tb_{7\cdot5}$	(74)
	1·48–4·64	Fl_D, $Tb_{7\cdot5}$	(74)
Air	1·53–4·5	17 ± 3° } Fl_D, $Tb_{2\cdot5}$	(78)
	1·50–	50°	
	1·44–4·75	100°	
	1·39–4·90	150°	
	1·34–5·05	200°	
	1·30–	250°	
	1·22–5·35	300°	

C_5H_{12} ISOPENTANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·30–	Centre ignit. E_V, sphere 16 cm. diam.	(30)

C_6H_6 BENZENE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·5 –	E_{2000}	(18)
Air	1·4 –4·7		(21)
Air	2·65–6·5	E_{110}	(23)
	1·4 –	Fl_D, $Tb_{6·2}$	(23)
Air	1·5 –8·0		(51)
Air	2·6 –7·2	E_{120}	(60)
O_2	2·6 –30·1	E_{120}	(60)
$O_2 : N_2$			(60)
40·5 : 59·5	–15·5	E_{120}	
58·0 : 42·0	2·6 –21·0	E_{120}	
78·5 : 21·5	–27·5	E_{120}	
Air	1·41–7·45 1·46–5·55	Fl_U } Wide tube Fl_D	(64)

C_6H_{14} HEXANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·3 –	E_{2000}	(18)

C_7H_8 TOLUENE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·3 –	E_{2000}	(18)
Air	1·4 –		(21)
Air	1·27–6·75 1·28–4·60	Fl_U } Wide tube Fl_D	(64)

C_7H_{18} HEPTANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·1 –	E_{2000}	(18)

C_8H_{18} OCTANE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	1·0 –	E_{2000}	(18)

PETROLEUM

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	2·4 – 4·9	E_{110}	(23)
	1·1 –	Fl_{D}, $\mathrm{Tb}_{6\cdot2}$	(23)
Air	2·94– 8·22	E_{V}, 60° fraction	(40)
Air	1·9 – 5·3	Fl_{D}, E_{100}	(48)
	1·5 – 6·4	Fl_{U}, E_{100}	(48)
	1·50–	23°	(48)
	1·42–	200°	(48)
	1·22–	300°	(48)
	1·02–	400°	(48)
Air	1·5 – 6·0	E_{2300}	(51)
Air	1·8 – 5·15	E_{120}	(60)
O_2	1·9 –28·8	E_{120}	(60)
$O_2 : N_2$			(60)
44·0 : 56·0	1·8 –14·1	E_{120}	
59·5 : 40·5	2·1 –19·2	E_{120}	
74·7 : 25·3	1·9 –28·8	E_{120}	

CH_4O METHYL ALCOHOL

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	5·5 –21·0		(51)
Air	7·8 –18·0		(21)
Air	6·0 –		(18)
Air	7·05–36·5	Fl_{U} Wide tube	(64)
	7·45–26·5	Fl_{D}	

C_2H_4O ACETALDEHYDE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	3·97–57·0	Fl_{U} Wide tube	(64)
	4·27–13·4	Fl_{D}	

C_2H_6O ETHYL ALCOHOL

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	3·07–		(18)
Air	4·0 –		(21)
Air	3·95–13·7	E_{110}	(23)
Air	4·0 –13·7		(29)
Air	2·8 –9·5		(51)
Air	3·56–18·0	Fl_U Wide tube	(64)
	3·74–11·5	Fl_D	
Air	5·02–	Fl_U $Tb_{2\cdot5}$, 60°	(57)
	5·18–	Fl_H	
	5·21–	Fl_D	
	4·24–19·0	Fl_U Tb_2, 60°	(57)
	4·32–13·8	Fl_H	
	4·44–11·5	Fl_D	
	4·16–	Fl_U Tb_{15}, 60°	(57)
	4·37–	Fl_H	
	4·23–	Fl_D	

C_3H_6O ACETONE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	2·9 –		(18)
Air	2·7 –		(21)
Air	5·0 –12·0		(29)
Air	2·15– 9·7	Fl_U	(52)
	2·35– 8·5	Fl_D	(52)
Air	2·3 – 7·5	Fl_U $Tb_{2\cdot5}$	(57)
	2·4 – 6·7	Fl_H	
	2·75– 6·5	Fl_D	
	2·2 – 9·5	Fl_U Tb_5	(57)
	2·25– 9·3	Fl_H	
	2·40– 8·3	Fl_D	
	2·15– 9·7	Fl_U Tb_{10}	(57)
	2·20– 9·5	Fl_H	
	2·35– 8·5	Fl_D	
	2·88–12·4	Fl_U Tb_{15}	(57)
	2·89–12·4	Fl_H	
	3·11–10·9	Fl_D	
Air	2·89–13·0	Fl_U Wide tube	(64)
	2·93– 8·6	Fl_D	
Air	3·59– 9·6	Glass pipette	(73)
	4·03– 8·5	Glass bulb	(73)
	3·68– 8·6	(20°) Iron tube	(73)
	3·30–10·1	100°	

C_3H_6O ALLYL ALCOHOL

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air	3·04–		(18)

C_3H_8O *n*-Propyl Alcohol

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	2·55–	E_{2000}	(18)

C_3H_8O Isopropyl Alcohol

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	2·65–	E_{2000}	(18)

C_4H_8O Ethylmethyl Ketone

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	1·97–10·1 2·05– 7·6	Fl_U Fl_D Wide tube	(64)

$C_4H_8O_2$ Ethyl Acetate

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	2·26–11·4 2·33– 7·1	Fl_U Fl_D Wide tube	(64)

$C_4H_{10}O$ Ether

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	1·9 –		(18)
Air - -	1·8 – 5·2		(21)
Air - -	2·75– 7·7	E_{110}	(23)
	1·6 –	Fl_D $\text{Tb}_{6\cdot2}$	(23)
Air - -	0·59–0·195*		(25)
Air - -	2·7 – 7·7		(29)
Air - -	2·35–18·5 2·38– 6·2 2·34– 6·3	Fl_U Fl_H Fl_D $\text{Tb}_{2\cdot5}$	(57) †
	1·93–15·8 2·05– 8·0 2·15– 6·2	Fl_U Fl_H Fl_D Tb_5, 20°	
	1·93–17·1 2·05–13·0 2·15– 7·5	Fl_D Fl_H Fl_D Tb_5, 60°	(57)
	1·73–23·3 1·93–22·3 1·80– 6·5	Fl_U Fl_H Fl_D Tb_{15}	(57)

* Gms. per litre.

† Cf. (94).

$C_4H_{10}O$ ETHER—*Continued*

Atm.	Limits.	Experimental Conditions.	Literature Ref.
	1·87–	P_{770}, $\mathrm{Fl_H}$	(57)
	–12·9	P_{751}, $\mathrm{Fl_H}$	(57)
	–10·5	P_{600}, $\mathrm{Fl_H}$	(57)
	– 9·2	P_{520}, $\mathrm{Fl_H}$	(57)
	1·88–	P_{460}, $\mathrm{Fl_H}$	(57)
	– 8·2	P_{450}, $\mathrm{Fl_H}$	(57)
	– 7·8	P_{400}, $\mathrm{Fl_H}$	(57)
	1·92– 7·3	P_{300}, $\mathrm{Fl_H}$	(57)
	2·08– 6·8	P_{200}, $\mathrm{Fl_H}$	(57)
	2·33– 6·1	P_{100}, $\mathrm{Fl_H}$	(57)
	2·99– 5·0	P_{50}, $\mathrm{Fl_H}$	(57)
	– 6·2	P_{600}, $\mathrm{Fl_D}$	(57)
	– 6·2	P_{300}, $\mathrm{Fl_D}$	(57)
	– 5·9	P_{200}, $\mathrm{Fl_D}$	(57)
	– 5·5	P_{100}, $\mathrm{Fl_D}$	(57)
		P_{50}	(57)
Air - -	1·71–48·0	$\mathrm{Fl_U}$ } Wide tube	(64)
	1·85– 6·4	$\mathrm{Fl_D}$	
Air - -	2·26– 6·90	Glass pipette	(73)
	2·38– 6·51	Glass bulb	(73)
	2·34– 6·15	(20°) } Iron tube	(73)
	1·97–	100°	
	1·63–	200°	

$C_4H_{10}O$ ISOBUTYL ALCOHOL

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	1·68–	E_{2000}	(18)

CS_2 CARBON DISULPHIDE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	1·94–		(18)
Air - -	4·1 –		(21)
Air - -	2·5 –45·0		(51)
Air - -	1·06–50·0	$\mathrm{Fl_U}$ } Wide tube	(64)*
	1·91–35·0	$\mathrm{Fl_D}$	
Air - -	2·11–31·7	Glass pipette	(73)
	2·22–31·2	Glass bulb	(73)
	3·38–29·2	(20°) } Iron tube	(73)
	1·35–33·1	100°	

C_2N_2 CYANOGEN

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	7·6 –38·0		(51)

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* Cf. (96).

C_5H_5N PYRIDINE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	1·81–12·4	Fl_U Wide tube	(64)
	1·88– 7·2	Fl_D	

$C_2H_5NO_3$ ETHYL NITRATE

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	3·01– 7·5	Fl_U Wide tube	(64)
	3·83–15·1	Fl_D	

WATER GAS (50 % H_2, 50 % CO)

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	12·5–66·5		(19)
Air - -	12·4–66·8	E_{110}, Sat.	(23)
	12·3–	Fl_D, $Tb_{6\cdot2}$	(23)

WATER GAS (49·45 H_2, 47·90 % CO, 2·65 % Air)

Atm.	Limits.	Experimental Conditions.	Literature Ref.
Air - -	12·4–66·2	E_{120}	(60)
O_2 - - -	12·6–92·1	E_{120}	(60)
$O_2 : N_2$ -			(60)
38·6 : 61·4 -	12·5–81·3	E_{120}	
52·7 : 47·3 -	12·6–86·1	E_{120}	

MIXTURES OF COMBUSTIBLE GASES (56). Cf. (50, 58, 66, 77), $E_{15{,}000}$, Fl_U

Composition by Volume.			Limits.
H_2	: CO	: CH_4	
100			4·1 –71·5
75	: 25		4·7 –
50	: 50		6·05–71·8
25	: 75		8·2 –
10	: 90		10·8 –
	100		12·5 –73·0
	90	: 10	11·0 –
	75	: 25	9·5 –
	50	: 50	7·7 –22·8
	40	: 60	7·2 –
	25	: 75	6·4 –
		100	5·6 –15·1
25	:	75	4·7 –
50	:	50	4·6 –
75	:	25	4·1 –
90	:	10	4·1 –
33	: 33	: 33	5·7 –29·9
55	: 15	: 30	4·7 –
48·5	:	51·5	–33·6

Relative Limiting Igniting Pressures † (6). Cf. (3, 5, 7, 8)

Below which, under the same sparking conditions, explosive mixtures would not ignite P = limiting ignition pressure in mm. Hg.

% H_2 in O_2	*P.*	% CO in O_2	*P.*
92·3	285	94·0	>400
91·7	341	93·9	75
88·9	212	92·5	108
85·7	183	91·0	99
80·0	149	88·9	81
75·0	123	85·7	78
66·7	103	80·0	55
50·0	66	75·0	50
40·0	53	66·7	50
36·7	53	50·0	30
33·3	45	40·0	26
25·0	52	37·5	24
16·7	54	35·3	27
11·8	57	33·3	32
9·1	72	25·0	74
8·8	68*	20·0	92
6·7	80*	18·4	106
		17·0	124
		16·0	135
		15·0	148
		14·3	340
		14·0*	
		13·8*	

Same as Above for Methane in Air (9)

Lower Limits.				Upper Limits.					
% CH_4 in Air.	Fl_D Tb_5 *P.*	% CH_4 in Air.	Fl_H Tb_5 *P.*	% CH_4 in Air.	Fl_D Tb_5 *P.*	% CH_4 in Air.	Fl_H Tb_5 *P.*	% CH_4 in Air.	Fl_U Tb_5 *P.*
5·75	760	5·39	760	13·38	760	15·11	745	14·28	734
5·80	455	5·41	575	13·35	545	13·94	405	13·94	485
5·90	315	5·51	380	13·23	330	13·59	300	13·59	340
5·99	270	5·70	320	12·89	240	13·23	260	13·23	290
6·12	180	5·75	285	12·21	180	12·89	210	12·89	240
6·48	90	5·90	215			12·21	160	12·21	170
		6·12	120						
		6·48	90						

* Incomplete combustion.

† Note separate list of literature references.

LITERATURE

(For a key to the periodicals, see pp. 534-535.)

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45 : 400 ; 26. ([89]) Jorissen, *29*, 22 : 291 ; 26. ([90]) Coward and Jones, *40*, 18 : 970 ; 26. ([91]) Coward and Hartwell, *3*, 1522 ; 26. ([92]) Rhead, *54*, 6 : 37 ; 27. ([93]) Tanaka and Najai, *24*, 2 : 280 and 494 ; 26. ([94]) White, *3*, 498 ; 27. ([95]) Berl and Werner, *19*, 40 : 245 ; 27. ([96]) White, *3*, 793 : 27.

Limiting Pressures

([1]) Meyer and Seubert, *4*, 45 : 581 ; 84. ([2]) Dixon, *2*, 175 : 634 ; 84. ([3]) De Hemptinne, *81*, 761 ; 02. ([4]) Fischer and Wolff, *7*, 44 : 2956 ; 11. ([5]) Coward, Cooper and Washburton, *3*, 101 : 2278 ; 12. ([6]) Coward, Cooper and Jacobs, *3*, 105 : 1069 ; 14. ([7]) Stavenhagen and Schuchard, *19*, 33 : 286 ; 20. ([8]) Stavenhagen and Schuchard, *19*, 34 : 114 ; 21. ([9]) Payman and Wheeler, *3*, 123 : 426 ; 23.

Relative Inflammabilities

([1]) Emich, *18*, 18 : 6 ; 97. ([2]) Emich, *18*, 19 : 299 ; 98.

4. PROPAGATION OF FLAME

The " Uniform Movement."

ABBREVIATIONS AND UNITS

Tb_x. A tube of diameter x cm. was used in experiment. The values given in the tables are the velocities of propagation of flame in cm./sec. for the mixtures noted. All gas percentages are in volume %.

(Much of the data is shewn graphically in Chapter XI.)

H_2 Hydrogen

Tb_1 (4). H_2 in Air.		(8). $2H_2+O_2+4N_2$		Tb_1 (7). $2H_2+O_2+4N_2$		$Tb_{2 \cdot 5}$ (41). Cf. (27). H_2 in O_2			
% H_2	cm./sec.	Tb_1	350	20°	350	% H_2	cm./sec.	% H_2	cm./sec.
20	200	$Tb_{0 \cdot 6}$	323	100°	430	10	64	77·5†	3170
25	280	$Tb_{0 \cdot 3}$	350			20	512	80·0	2280
30*	340	$Tb_{0 \cdot 09}$	172			24·2	845	81·6	1930
35	410	$3H_2+Cl_2$				29·5	1200	82·9	1440
40	440	Tb_1	315			33·8	1620	87·5	730
50	380	H_2+3Cl_2				39·2	2220	89·4	530
60	230	Tb_1	600			48·5	3150	93·5	7615
						52·6†	3680	94·4	—

* Not propagated in $Tb_{0 \cdot 09}$ or less.

† The speeds of mixtures between these were found to be variable.

H_2 in air (16). (Cf. 45) *A*, in $Tb_{0\cdot9}$; *B*, in $Tb_{1\cdot5}$; *C*, in $Tb_{2\cdot5}$.

% H_2	*A*	% H_2	*B*	% H_2	*C*	
11·80	No	17·30	150	6·10	No	(23)
17·30	125	25·15	260	6·19	10	
23·65	200	33·90	383	6·31	12	
30·45	320	37·15	400	20·15	260	(16)
36·55	390	40·10	410	29·70	405	
40·10	420	43·10	420	36·30	490	
43·10	420	46·80	400	40·50	480	
46·80	400	51·55	360	44·55	460	
50·55	353	57·15	270	49·15	385	
57·00	280	59·45	175	61·60	145	
62·00	155			71·39	50	(23)
63·50	No			71·51	*	

* Flame to open end only.

CO CARBONIC OXIDE

$Tb_{2\cdot5}$ (23) CO in Air, saturated with H_2O at room temp. and $P=1$ atm.

% CO.	cm./sec.
16·15	*
16·29	19·5
16·51	19·4
24·47	34·0
30·50	46·0
44·84	60·1
59·58	56·2
67·10	30·2
70·63	20·0
71·19	19·4
71·31	†

Effect of H_2 and H_2O on flame speeds of CO – air mixtures (33)

t°	% CO	% H_2	% H_2O	cm./sec.
6	39·25	0·65	1·90	73·5
28	38·00	0·65	3·70	103·5
4	39·70	1·90	0·80	103·5
6	46·15	3·85	0·90	152·0
10	47·30	4·05	1·20	150·0
29	46·00	4·05	3·95	167·0
20	47·30	4·15	2·30	144·0
5	37·45	5·60	0·85	170·0
6	43·75	5·60	0·90	170·5
31	42·20	5·60	44·0	156·0
6	40·80	6·05	0·90	160·5
27	39·60	6·05	3·50	158·0

Tb (7)
$2CO+O_2$, 220 cm./sec.

* Flame tongue. † Flame to 15 cm.

Effect of H_2O on flame-speed (33). $Tb_{2\cdot5}$ *t*° = temp. of saturation with H_2O.

t°	% H_2O	cm./sec.	*t*°	% H_2O	cm./sec.	*t*°	% H_2O	cm./sec.
2*	0·70	56	42*	8·00	118	27†	3·50	96
13*	1·45	76	4†	0·80	56	34†	5·20	107
27*	3·50	106	12†	1·35	68	39†	6·85	107
34*	5·20	120	20†	2·30	86			

* = 45 % CO in air. † = 40 % CO in air.

CH_4 METHANE

CH_4 in air (12); Cf. (3, 6, 7, 8). *A* in glass $\text{Tb}_{2\cdot65}$; *B* in lead $\text{Tb}_{2\cdot64}$; *C* in copper $\text{Tb}_{2\cdot2}$; *D* in iron $\text{Tb}_{2\cdot72}$;					CH_4 in Air (13) Tb_5	
% CH_4	*A*	*B*	*C*	*D*	% CH_4	cm./sec.
5·99	21·7	19·4	18·3	21·2	5·4	36
6·83	33·4	32·5	32·7	34·1	6·8	55
7·6	45·6	43·5	42·4	43·8	8·8	100
7·95	48·6	48·2	45·2		9·45	110
8·94	63·66	58·7	59·4	63·3	10·6	109
10·0	69·8	65·0	63·2	67·3	11·5	84
10·98	61·1	53·9	54·1	57·5	13·0	42
11·3	53·3	45·4	47·7	50·6	14·3	36
11·74	36·9	35·2	34·5	36·1		

"Uniform movement" velocities in tubes of small diameter (20). *D* = internal diam. of tube in mm.; % = % CH_4 in air.

D \ %	7·6	8·0	8·25	8·4	8·5	9·0	9·5	9·95	10·15
3·6	0	0	0	0	0	0	0	0	0
4·5	0	0	(20)	(18)	(20)	(20)	(20)	(33)	0
5·6	(25)	(20)	(27)	—	36·3	38·4	40·8	41·2	40·8
7·2	(37)	(30)	(30)	(30)	38·0	40·5	46·8	46·3	44·5
8·1	(45)	(30)	(35)	36·5	39·3	42·4	47·7	47·4	46·7
9·0	(55)	32·6	34·8	—	40·4	44·4	48·9	48·0	47·9

D \ %	10·5	10·65	10·8	11·0	11·5	11·6	11·65	12·0
3·6	0	0	0	0	0	0	0	0
4·5	0	0	0	0	0	0	0	0
5·6	38·4	0	0	0	0	0	0	0
7·2	42·9	(60)	(53)	(43)	0	0	0	0
8·1	44·0	42·2	41·0	(45)	(50)	—	—	(60)
9·0	46·5	45·5	—	42·5	36·9	35·3	(69)	(60)

Figures in brackets denote distance travelled before flame died out.

METHANE (*continued*)

CH_4 in Air, $Tb_{2\cdot5}$ (23).		CH_4 in O_2 (27).	
% CH_4	cm./sec.	% CH_4	cm./sec.
5·71	*	5·59	†
5·80	23·3	5·72	20
6·95	35·0	10·52	266
7·82	47·4	15·53	722
9·12	64·4	21·63	2300
9·96	66·2	26·95	3991
10·32	65·5	33·00	5502
11·10	57·0	40·00	3020
12·25	35·0	45·61	488
13·09	22·0	53·36	82
13·35	19·1	57·67	29
13·42	†	59·50	‡

* Flame to 15 cm. † Flame to 5 cm. ‡ Flame to 30 cm.

C_2H_2 ACETYLENE

C_2H_2 in Air.		C_2H_2 in Air.		C_2H_2 in Air (22)					C_2H_2 in O_2 (41)	
Tb_4 (9)		$Tb_{1\cdot2}$ (18)		% C_2H_2	Diam. of Tube in mm.				% C_2H_2	$Tb_{2\cdot5}$
% C_2H_2	cm./sec.	% C_2H_2	cm./sec.		12·5	25	50	90		cm./sec.
2·9*	10	4	45	2·75				40	3·5	44·2
8·0	500	6	147	3·45	25	41	60		4·7	222
9·9–10·0	600	8	260	4·40				115	7·4	970
22·0	40	9	266	4·60	82	95	115		9·1	1463
64*	5	10	264	6·10	158	172	205		10·9	2185
		12	175	7·00				265	11·9†	2480
		14	114	8·15	258	270	303		63·5†	2070
		16	75	9·45				335	64·5	1440
		18	50	10·35	260	278	304		66·0	880
		20	38	11·6	206	245	283		70·5	350
				11·85				285	74·5	122
				13·25	115	145	175	220	81·4	46·0
				16·00	60	68	72		85·0	32·0
				18·20			60	70	87·9	22·5

* Limit mixtures. † The flame movements of mixtures between these were not uniform.

C_2H_4 ETHYLENE				C_2H_6 ETHANE		C_3H_8 PROPANE		C_4H_{10} BUTANE	
In Air (29)		In O_2 (41)		In Air (23)		In Air (23)		In air (23)	
$Tb_{2\cdot5}$ % C_2H_4	cm./sec.	$Tb_{2\cdot5}$ % C_2H_4	cm./sec.	$Tb_{2\cdot5}$ % C_2H_6	cm./sec.	$Tb_{2\cdot5}$ % C_3H_8	cm./sec.	$Tb_{2\cdot5}$ % C_4H_{10}	cm./sec.
3·55	25·8	5·3	130	3·16	*	2·30	‡	1·90	‖
4·00	41·3	7·5	635	3·30	18·1	2·37	20·8	1·95	20·1
6·10	108·4	10·0	1065	3·58	25·6	2·58	26·0	2·05	23·3
6·50	129·9	12·4	2560	4·47	52·7	2·80	31·4	2·57	49·1
7·20	142·2	**15·4	3980	4·90	65·0	3·50	48·2	3·01	67·9
8·10	120·6	**40	2900	5·57	80·5	4·28	72·8	3·40	80·2
9·45	72·6	43·2	1430	6·08	82·5	4·39	79·1	3·66	82·6
13·35	23·5	45·6	854	6·53	85·6	4·71	82·1	4·05	75·0
14·00	22·2	48·0	430	7·07	81·3	4·84	80·2	4·34	61·9
		53·1	116·0	7·70	60·4	5·14	66·0	4·88	43·4
		55·45	76·0	8·23	45·8	5·90	41·2	5·50	27·7
		57·9	53·0	9·00	27·7	6·58	30·2	6·27	22·0
				9·50	23·1	7·10	23·0	6·53	20·3
				10·09	20·8	7·30	20·3	6·60	¶
				10·60	19·7	7·35	§		
				10·71	†				

* Flare only. † Flame to 4 cm. ‡ Flame to 6 cm.
§ Flame to 15 cm. ‖ Flame to 6 cm. ¶ Flame to open end only.
** The flame movements of mixtures between these were not uniform.

C_5H_{12} PENTANE				C_3H_6O ACETONE		$CS_2 + 3NO$	
In Air (23). $Tb_{2\cdot5}$				In Air (17)		Cf. (5, 8)	
% C_5H_{12}	cm./sec.	% C_5H_{12}	cm./sec.	$Tb_{2\cdot5}$			
1·52	*	3·85	48·0	%C_3H_6O	cm./sec.		
1·61	20·2	4·00	44·0	2·70	55·0	Tb_3	125
1·98	40·1	4·32	33·0	3·85	69·0	Tb_2	124
2·35	60·2	4·56	28·7	5·05	93·8	Tb_1	75
2·63	74·3	4·87	25·8	6·40	68·5	$Tb_{0\cdot4}$	—
2·92	83·0	5·40	20·2	7·65	39·5		
3·00	82·1	5·50	†	8·20	30·5		
3·13	76·0						
3·35	65·9						
3·49	61·5						

* Flame to 6 cm. † Flame to open end only.

LITERATURE

(For a key to the periodicals, see pp. 534-535.)

(1) Bunsen, *16*, 131: 161; 67. (2) Mallard, *9*, 7: 355; 75. (2a) Guoy, *6*, (v.) 18: 1; 79. (3) Fonseca Benevides, *55*, 7: 166; 80. (4) Mallard and Le Chatelier, *5*, 93: 145; 81. (5) Mallard and Le Chatelier, *5*, 95: 599; 82. (6) Mallard, *56*, 15: 268; 82. (7) Mallard and Le Chatelier, *15*, 1: 173; 82. *14*, 39: 369, 572; 83. (8) Mallard and Le Chatelier, *9*, 4: 296; 83. (9) Le Chatelier, *5*, 121: 1144; 95. (10) Bunte, *7*, 31: 19; 98. (10a) Andrade, *10*, 37: 380; 12. (11) Sellars and Campbell, *21*, 32: 730; 13. (12) Parker and Rhead, *3*, 105: 2150; 14. (13) Wheeler, *3*, 105: 2606; 14. (14) Morgan, *31*, 99: 39; 15. *36*, 26: 172; 14. (15) Parker, *3*, 107: 328; 15. (16) Haward and Otagawa, *3*, 109: 83; 16. (17) Wheeler and Whitaker, *3*, 111: 267; 17. (18) Haward and Sastry, *3*, 111: 841; 17. (19) Mason and Wheeler, *3*, 111: 1044; 17. (20) Payman and Wheeler, *3*, 113: 656; 18. (21) Payman and Wheeler, *3*, 115: 36; 19. (22) Mason and Wheeler, *3*, 115: 578; 19. (23) Payman, *3*, 115: 1446, 1454; 19. (24) Morgan, *31*, 108: 535; 19. (25) Nickolls, *Underwriters Labs. Special Investigation*, No. 528; 19. (25a) Hofsass, *8*, 62: 541; 19. (26) Mason and Wheeler, *3*, 117: 36; 20. (27) Payman, *3*, 117: 48; 20. (28) Mason and Wheeler, *3*, 117: 1227; 20. (29) Chapman, *3*, 119: 1677; 21. (30) Payman and Wheeler, *3*, 121: 363; 22. (30a) Payman, *54*, 2: 110; 23. (31) Mason, *3*, 123: 210; 23. (32) Payman, *3*, 123: 412; 23. (33) Payman and Wheeler, *3*, 123: 1251; 23. (34) Ellis, *3*, 123: 1435; 23. (35) Campbell and Ellis, *3*, 125: 1957; 24. (36) Ellis and Stubbs, *3*, 125: 1960; 24. (37) Ellis and Robinson, *3*, 127: 760; 25. (38) Ellis and Wheeler, *3*, 127: 764; 25. (39) Chapman and Wheeler, 3: 2139; 26. (40) Payman and Wheeler, *29*, 22: 301; 26. (40a) Stevens, *13*, 48: 1896; 26. (41) Bone, Fraser and Winter, *1*, 114: 402; 27. (42) Bone, Fraser and Winter, *1*, 114: 420; 27. (43) Bone, Fraser and Witt, *1*, 114: 442; 27. (44) Chapman and Wheeler, *3*, (1927); 38. (45) Georgeson and Hartwell, *3*, 1927: 265. (46) Coward and Jones, *13*, 49: 386; 27. (47) Coward and Jones, *52*, No. 2757; 27.

Theoretical Papers

(1) Vicaire, *6*, (iv), 19: 118; 70. (2) Mallard and Le Chatelier, *9*, 4: 296; 83. (3) Jouget, *5*, 156: 872; 13. (4) Nusselt, *20*, 59: 872; 15. (5) Jouget and Crussard, *5*, 168: 820; 19.

5. DETONATION

ABBREVIATIONS

Values not otherwise designated are detonation velocities in metres per second.

Composition of gas mixtures when given in percentages are in volume %.

The initial conditions of the detonating mixture are ordinary temperature and pressure unless otherwise stated.

H_2 HYDROGEN

Determinations in rubber tube 40 m. long × 5 mm. diam. ([3]).

$2H_2+O_2$, Normal conditions, 2810				% ($2H_2+O_2$). In Air.		% H_2 in Air.	
P_{mm}	m./sec.	P_{mm}	m./sec.			30·0	1439
560	2763	1260	2776	45	1439	26·7	1201
760	2800	1580	2744	40	1251	23·3	1205
$2H_2+N_2O$		2284		35	1205	21·7	*
$2H_2+N_2+O_2$		2121		32·5	*		

Determinations in a lead 100 m. long × 6 mm. diam. ([8]).

For $2H_2+O_2$, normal conditions, 2821.

At 10°				At 100°			
P_{mm}	m./sec.	P_{mm}	m./sec.	P_{mm}	m./sec.	P_{mm}	m./sec.
200	2627	760	2821	300	2697	1000	2828
300	2705	1100	2856	500	2738	1450	2842
500	2775	1500	2872	760	2790		

$2H_2+O_2$	2821	$2H_2+8O_2$	1281	$2H_2+O_2+N_2$	2426
$2H_2+2O_2$	2328	$4H_2+O_2$	3268	$2H_2+O_2+3N_2$	2055
$2H_2+4O_2$	1927	$6H_2+O_2$	3527	$2H_2+O_2+5N_2$	1822
$2H_2+6O_2$	1707	$8H_2+O_2$	3532	$2H_2+2O_2+2N_2$	2003

H_2+N_2O	2305	$3H_2+N_2O$	2705	$H_2+N_2O+N_2$	1991
$2H_2+N_2O$	2545	$7H_2+2N_2O$	2732	$2H_2+2N_2O+3N_2$	1880

H_2+N_2O, at $P_{mm}=500$, 2094 ; $P_{mm}=760$, 2307 ; $P_{mm}=1000$, 2302.

* Detonation not propagated.

Determinations in a lead pipe 100 m. long × 9 mm. diam. (24).

% H_2	% O_2	m./sec.	% H_2	% O_2	m./sec.	% H_2	% O_2	m./sec.
22·2	77·8	1600	50·0	50·0	2311	85·5	14·5	3527
25·0	75·0	1693	66·7	33·3	2817	88·9	11·1	3532
33·3	66·7	1917	80·0	20·0	3278			

% H_2	% O_2	% N_2	m./sec.	% H_2	% O_2	% N_2	m./sec.
25·0	50·0	25·0	1756	33·3	33·3	33·3	1990
33·3	44·4	22·3	1961	50·0	25·0	25·0	2388
50·0	33·3	16·7	2374	66·6	16·7	16·7	2767
66·6	22·2	11·2	2822	75·0	12·5	12·5	2846
75·0	16·7	8·3	3090	33·3	26·6	40·1	2016
80·0	13·3	6·7	3137	50·0	20·0	30·0	2383
				66·6	13·3	20·1	2655
				71·4	11·4	17·2	2671

In Glass Tubes (22)				(8)		H_2+Cl_2 in dark, dry 1795 wet, 1770 (6).
Tube diam. =	9	12·7	15			
$2H_2+O_2$	2821		2828	H_2+Cl_2	1729	
$2H_2+4O_2$	1927	1921		$2H_2+Cl_2$	1849	
$2H_2+O_2+3N_2$	2055		2089	$3H_2+Cl_2$	1855	

NH_3 AMMONIA (8).

$4NH_3+3O_2$, 2390. $2NH_3+N_2O$, 2200.

ClO_2 CHLORINE PEROXIDE

53·5 % ClO_2, 46·5 % O_2, 1065. 64·0% ClO_2, 36·0 % O_2, 1126 (11).

CO CARBONIC OXIDE

(3)			
$2CO+O_2$		$CO+N_2O$ 1106 $\left.\begin{array}{l}2CO+O_2\\+2N_2\end{array}\right\}$ (1000) 30 % CO in air not detonated.	$2CO+O_2$ (13). In CO mixtures the speed may be influenced by nature of igniting charge. Fired by 0·10 g. chlorate powder - - - 1280* 0·05 g. fulminate - 1900† 0·75 g. fulminate - 1210‡
P_{mm}	m./sec.		
570	1120		
760	1089		
834	1072		
1560	1132		

* Wave-variable. † Explosive. ‡ Undulatory.

$2CO+O_2$; influence of H_2O vapour (8) ; $t°$ = saturation temp.

$t°$	% H_2O	P_{mm}	m./sec.	$t°$	% H_2O	P_{mm}	m./sec.
	Well-dried		1264	35	5·6	760	1738
	Dry		1305	35	5·6	1100	1782
10	1·2		1676	45	9·5	400	1570
20	2·3	400	1576	45	9·5	760	1693
20	2·3	670	1703	45	9·5	1100	1742
20	2·3	1100	1737	55	51·6		1666
28	3·7		1713	65	24·9		1526
35	5·6	400	1616	75	38·4		1266

CH_4 METHANE

(8)				In O_2 (24)		(3)	
CH_2+2O_2		CH_4+2O_2	2146	% CH_4		CH_4+2O_2	2287
P_{mm}	m./sec.	CH_4+4O_2	1963	11·1	1678	CH_4+2N_2 $+4O_2$	1858
500	2280	$CH_4+1\frac{1}{2}O_2$ $+\frac{1}{2}N_2$	2349	20·0	1980	CH_4+4N_2 $+2O_2$	1151
760	2322	$CH_4+1\frac{1}{2}O_2$ $+1\frac{1}{2}M_2$	2154	25·0	2146	$CH_4+7{\cdot}52\ N_2+2O_2$ gives no detonation	
1000	2319	$CH_4+1\frac{1}{2}O_2$ $+2\frac{1}{2}N_2$	1880	33·3	2337		
CH_4 + $1\frac{1}{2}O_2$				40·0	2465		
500	2418			50·0	2513		
760	2470			53·3	2388		
1000	2588						

C_2H_2 ACETYLENE

(13)				(8)	
$2C_2H_2+O_2$	2160	$C_2H_2+6O_2$	1950	$C_2H_2+2\frac{1}{2}O_2$	2391
$1\frac{1}{2}C_2H_2+O_2$	2510	$C_2H_2+10O_2$	1850	$C_2H_2+1\frac{1}{2}O_2$	2716
$C_2H_2+O_2$	2920	$C_2H_2+2N_2O$	2580	$C_2H_2+1\frac{1}{2}O_2+N_2$	2414
$C_2H_2+3O_2$	2220	$C_2H_2+6N_2O$	2400	$C_2H_2+O_2$	2961 (16)
$C_2H_2+4O_2$	2190	C_2H_2+2NO	2850	$C_2H_2+2\frac{1}{2}O_2$	2482 (3)
		C_2H_2+6NO	2800		

98 % C_2H_2 (12). Determinations made in tube 1 m. long × 3·5 mm. diam. Since C_2H_2 is an endothermic compound, it can be detonated under pressure.

P = initial detonating pressure in kg./cm².

P - - -	5	10	12	15	20	30
Speed - - -	1050	1100	1280	1320	1500	1600

C_2H_4 ETHYLENE

(8)					
$C_2H_4+2O_2$*	2581	$C_2H_4+6O_2$	2118	$C_2H_4+2O_2+2N_2$	2211
$C_2H_4+2O_2$†	2538	$C_2H_4+8O_2$	1980	$C_2H_4+2O_2+4N_2$	2024
$C_2H_4+3O_2$	2364	$C_2H_4+10O_2$	1856	$C_2H_4+2O_2+6N_2$	1878
$C_2H_4+4O_2$	2247	$C_2H_4+2O_2+N_2$	2413	$C_2H_4+2O_2+8N_2$	1734
(3)					
$C_2H_4+3O_2$	2209				

* 10°. † 100°.

C_2H_6 ETHANE

$C_2H_6+3\frac{1}{2}O_2$, 2363 (3).

C_2N_2 CYANOGEN

(3)	
$C_2N_2+4N_2O$	2035
$C_2N_2+2O_2$	2043
$C_2N_2+2N_2+2O_2$	1203
$C_2N_2+4N_2+2O_2$	*

P_{mm}	$C_2N_2+2O_2$
388	2171
758	2195
878	2052

(8)		
P_{mm}	$C_2N_2+O_2$	
500	2536	$C_2N_2+2O_2$, 2321
760	2677	$C_2N_2+3O_2$, 2110
1000	2671	$C_2N_2+O_2+N_2$, 2398
$t°$		$C_2N_2+O_2+N_2$, 2165
10	2728	
100	2711	

(22)	
$C_2N_2+O_2+2N_2$	
Diam. of tube.	m./sec.
6 mm.	2161
9 mm.	2230
12·7 mm.	2230

* Detonation not propagated.

C_2H_6O ETHYL ALCOHOL

(20a).

(C_2H_6O) - -	$+1\frac{1}{2}O_2$ 2396	$+2O_2$ 2433	$+3O_2$ 2356	$+6O_2$ 2068	$+8O_2$ 1942	$+15O_2$ 1646
$(C_2H_6O+3O_2)$ - (2356)	$+3N_2$ 2108	$+5N_2$ 2006	$+12N_2$ 1690			

C_5H_{12} PENTANE

(20a).

(C_5H_{12}) - -	$+4O_2$ 2580	$+6O_2$ 2518	$+8O_2$ 2371	$+12O_2$ 2140	$+16O_2$ 2050	$+32O_2$ 1780	$+40O_2$ 1690
$(C_5H_{12}+8O_2)$ (2371)	$+4N_2$ 2114	$+8N_2$ 1987	$+24N_2$ 1680	$+32N_2$ —			

C_6H_6 BENZENE

(20a).

(C_6H_6) -	$+3O_2$ 2380	$+4O_2$ 2527	$+6O_2$ 2342	$+7\frac{1}{2}O_2$ 2206	$+12O_2$ 2062	$+15O_2$ 1982	$+30O_2$ 1758	$+40O_2$ 1647
$(C_6H_6+7\frac{1}{2}O_2)$ (2206)	$+4\frac{1}{2}N_2$ 2100	$+7\frac{1}{2}N_2$ 1991	$+22\frac{1}{2}N_2$ 1658	$+26N_2$ —				

$C_4H_{10}O$ ETHER

(20a).

$(C_4H_{10}O)$ - -	$+2O_2$ 2212	$+4O_2$ 2542	$+6O_2$ 2400	$+10O_2$ 2140	$+3O_2$ 1697
$(C_4H_{10}O+6O_2)$ (2400)	$+24N_2$ 1698				

CS_2 Carbon Disulphide—See page 418.

MIXTURES OF COMBUSTIBLE GASES

(23)

$2(xH_2+yCO)+O_2$			$4(xH_2+yCO)+O_2$		
x	*y*	m./sec.	*x*	*y*	m./sec.
0·75	99·25	1754	1	99	1747
1·5	98·5	1758	2	98	1755
7·5	92·5	1796	5	95	1776
15	85	1858	25	75	1952
37·5	62·5	2020	50	50	2212
50	50	2130	75	25	2614
75	25	2391	85	15	2819
85	15	2507	92·5	7·5	3015
92·5	7·5	2643	100	0	3284
100	0	2810			

H_2+CH_4 (24). $M=\%$ mixture in O_2

H_2+CH_4		$2H_2+CH_4$		H_2+2CH_4	
M	m./sec.	*M*	m./sec.	*M*	m./sec.
13·8	1532	14·3	1449	14·3	1728
21·0	1875	15·8	1582	25·0	2050
44·4	2464	16·7	1666	40·0	2444
50·0	2561	20·0	1764	46·1	2546
57·1	2697	33·3	2094	50·0	2605
66·7	2604	50·0	2474	54·5	2679
		54·5	2572	60·0	2600
		66·7	2782		

(8)	
$2H_2+O_2+2CO$	2455
$2H_2+O_2+6CO$	2080
H_2+O_2+2CO	2143
(3)	
H_2+O_2+CO	2008
$3H_2+2\frac{1}{2}O_2+2CO$	2170
(3)	
$H_2+C_2H_4+3\frac{1}{3}O_2$	2417
$2H_2+C_2H_4+4O_2$	2579
(3)	
$H_2+C_2H_6+4O_6$	2250

LIMITING DILUTIONS OF EXPLOSIVE MIXTURES FOR THE INITIATION OF DETONATION

Detonation cannot be propagated in mixtures diluted beyond the limits given.

Mixture.	Limits.		Lit.
H_2 and air - -	Lower Limit between 23·3 % and 21·7 %	1205	(3)
	Lower Limit between 18 % and 19 %	1300	(30)
CO - - -	$4CO + 2N_2 + O_2$	*	(3)
	$2CO + N_2 + O_2$	*	(3)
CO and O_2 - -	Lower limit between 38 % and 39 %	1250	(30)
CH_4 Methane and O_2	Lower Limit 11·1 % CH_4	1678	
	Upper Limit 53·3 % CH_4	2388	(24)
	$CH_4 + 4N_2 + 2O_2$	1151	(3)
	$CH_4 + 7{\cdot}5N_2 + 2O_2$	*	(3)
	9·5 % CH_4 in air	*	(3)
C_2H_2 Acetylene -	$C_2H_2 + 10O_2$	1850	(13)
	$C_2H_2 + 6NO$	2800	(13)
C_2N_2 Cyanogen -	$C_2N_2 + 2N_2 + 2O_2$	1203	(3)
	$C_2N_2 + 4N_2 + 2O_2$	*	(3)
	$C_2N_2 + 4N_2O$	2035†	(3)
	$C_2N_2 + 4NO$	*	(3)

* Detonation not propagated. † Sometimes propagated.

Mean flame velocity before a uniform detonation speed ensues (3). $2H_2 + O_2$, in rubber tube 5 mm. diam.; D = m. from initiating explosive; S = time in sec.; V = mean vel. from origin in m./sec.; $V_{\text{int.}}$ = mean vel. in each interval.

D	S	V	$V_{\text{int.}}$
0·020	0·000275	72·72	72·7
0·050	0·000342	146·2	448·0
0·500	0·000541	924·4	2261
5·250	0·002108	2491·0	3031
20·190	0·007620	2649·0	2710
40·430	0·015100	2679·0	2706

Distance in inches from spark at which detonation occurs = D_0 for spark at end of tube and D_3 for spark 3 in. from end (16).

Mixture	D_0	D_3
$2H_2 + O_2$	48	12
$2H_2 + 2\frac{1}{2}O_2$		48
$6H_2 + O_2$		192
$C_2N_2 + O_2$	$8\frac{1}{2}$	4
$C_2N_2 + 2O_2$	12	10
$2C_2H_2 + 3O_2$	$4\frac{1}{2}$	$2\frac{1}{2}$
$C_2H_4 + 2O_2$	9	5

Distance before detonation wave is established $= D$ cm. ([13]). Glass tube, 10 mm. diam. Spark at end of tube.

Mixture	D
$2C_2H_2 + O_2$	100
$C_2H_2 + O_2$	5
$C_2H_2 + 6O_2$	15
$C_2H_2 + 10O_2$	80
$C_2H_2 + 2NO$	20
$C_2H_2 + 6NO$	50
$C_2H_2 + 2N_2O$	100
$C_2H_2 + 6N_2O$	10

Influence of tube diameter on the distance from the firing source at which detonation occurs ([25]).§ Mixture $= CS_2 + 3O_2$. Spark at end of tube. $D_{cm} =$ cm. travelled by flame before detonation.

Tube diam. mm.	D_{cm}
6·5–7	48
10	50
24–25	58
34–35	84
43–44	103
53–54	131

Distance required for the re-establishment of detonation waves after being damped out by passing from one tube to another of larger diameter ([26]). Diam. of first tube $= 7$ mm. Distance in cm. travelled by flame in second tube prior to detonation $= D$.

Diam. mm. second tube	13	16	23–24	33–34	44–45
D ($CS_2 + 3O_2$)	8	10	15	50	100
D ($2H_2 + O_2$)			3	62	

WAVE VELOCITIES ([14])

	$C_2H_2 + O_2$	$C_2H_2 + 2NO$	$2CO + O_2$
L'onde explosive (detonation wave)	2990	2850	1900
L'onde retrograde (retonation wave)*	2300	1140	
L'onde reflechie (reflexion wave)†	2250	1350	1000
L'onde prolongee (collision wave)‡	2050		

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* A "retonation" wave is thrown back into the burnt gases when the detonation wave is set up.

† The wave reflected through the burnt gases after a detonation wave has reached the walls of the vessel in which the explosion occurs.

‡ Collision waves occur when two detonation waves meet.

§ Cf. page 187.

REFLECTED WAVES IN A $C_2H_2+O_2$ MIXTURE

Initial speed - - -	2300	After first crossing -	1080
After reflection - -	1350	After second crossing -	980

RATIO OF WAVE VELOCITIES (16)

Mixture.	Detonation Wave Velocity.	Reflection Wave Velocity.	Ratio of Velocities.
$2H_2+O_2$	2820	1538	1·83
H_2+N_2O	2305	1383	1·67
$2CO+O_2$	1676	1078	1·56
$C_2N_2+O_2$	2728	1230	2·22
$C_2N_2+2O_2$	2391	1129	2·06
$2C_2N_2+5O_2$	2391	1133	2·11

For theoretical formulae for the calculation of detonation velocities, see pages 180 to 186.

LITERATURE

(For a key to the periodicals, see pp. 534-535.)

EXPERIMENTAL

(1) Berthelot, *5*, 93: 18; 81. (2) Mallard and Le Chatelier, *5*, 93: 145; 81. (3) Berthelot and Vieille, *5*, 94: 101; 82. 95: 151, 199; 82. *6*, 28: 289; 83. *14*, 40: 353; 83. (4) Von Oettingen and Von Gernet, *10*, 33: 586; 88. (5) Dixon and Smith, *25*, 2: 2; 89. (6) Dixon and Harker, *25*, 3: 118; 90. (7) Lean and Bone, *11*, 1892: 673. (8) Dixon, *2*, 184: 97; 93. (9) Dixon and Cain, *25*, 8: 180; 94. (10) Dixon, Strange and Graham, *3*, 69: 759; 96. (11) Dixon and Harker, *3*, 69: 789; 96. (12) Berthelot and Le Chatelier, *5*, 129: 427; 99. (13) Le Chatelier, *6*, 20: 15; 00. *5*, 130: 1755; 00. (14) Le Chatelier, *5*, 131: 30; 00. (15) Jones and Bower, *25*, 42: No. 7; 98. (16) Dixon *et al*, *2*, 200: 345; 03. (17) Dixon and Bradshaw, *1*, 79: 234; 07. (18) Bradshaw, *1*, 79: 236; 07. (19) Dixon, *3*, 99: 588; 11. (20) Dixon, Campbell and Slater, *1*, 90: 506; 14. (20a) Dixon, *B* 2: 20. (21) Dutcher, *57*, 15: 228; 20. (22) Campbell, *3*, 121: 2483; 22. (23) Dixon and Walls, *3*, 123: 1025; 23. (24) Payman and Walls, *3*, 123: 420; 23. (25) Laffitte, *5*, 176: 1392; 23. (26) Laffitte, *5*, 177: 178; 23. (27) Evreinoff, *Journal des Mines* (Russie), No. 2; 23. (28) Audibert, *5*, 178: 1275; 24. (29) Laffitte, *5*, 179: 1394; 24. (30) Wendlandt, *17*, 110: 637; 24. (31) Malinowski, *15*, 21: 468; 24. (32) Wendlandt, *17*, 116: 227; 25. (33) Laffitte, *6*, 4: 587; 25. (34) Payman and Robinson, *28*, 18: 26. (35) Payman and Shepherd, *28*, 29: 26. (36) Laffitte and Dumanois, *5*, 183: 284; 26. (37) Campbell and Woodhead, 3: 3010; 26. (38) Dixon and Campbell, *29*, 22: 307; 26. (39) Egerton and Gates, *1*, 114: 137; 27.

THEORETICAL

(1) Berthelot, *5*, 94: 149; 82. 96: 672; 83. (2) Chapman, *4*, 47: 90; 99. (3) Vieille, *58*, 10: 177; 99. *5*, 131: 413; 00. (4) Jouget, *5*, 134: 1418; 02. 135: 778; 02. 138: 1685; 04. 139: 121, 786; 04. 140: 711; 05. 142: 831, 1034;

06. *408*, 1 : 347 ; 05. 2 : 5 ; 06. (5) Zemplin, *5*, 141 : 710 ; 05. (6) Jouget, *5*, 144 : 415 ; 07. (7) Crussard, *5*, 144 : 417 ; 07. (8) Crussard and Jouget, *5*, 144 : 560 ; 07. (9) Jouget, *5*, 144 : 632 ; 07. (10) Crussard, *59*, 6 : 297 ; 07. *(11)* Jouget, *5*, 146 : 915 ; 08. (12) Jouget and Crussard, *5*, 146 : 954 ; 08. (13) Jouget *5*, 150 : 91 ; 10. (14) Crussard, *5*, 156 : 447, 611 ; 13. (15) Jouget, *5*, 156 : 872, 1058 ; 13. (16) Crussard, *5*, 158 : 125 ; 14. (17) Jouget and Crussard, *5*, 168 : 820 ; 19. (18) Crussard, *60*, 12 : 243, 295 ; 20. (19) Vautier, *5*, 179 : 256 ; 24. (20) Jouget, *5*, 181 : 546 ; 25. (21) Jouget, *5*, 181 : 658 ; 25. Also Jouget, *Mecanique des Explosifs*, Paris, 1917.

6. EXPLOSIONS IN CLOSED VESSELS

Much of the experimental determination of explosion times and pressures using gaseous mixtures has been carried out with coal gas—air mixtures. Owing to the variable composition and heat of combustion of the samples of coal gas so employed, it has not been found possible to tabulate such data except in so far as it may have a general bearing on the subject of gaseous explosions—and more particularly where data relative to the simpler combustible gases is lacking.

All maximum pressures have been expressed as a ratio, $\frac{\text{maximum pressure}}{\text{initial pressure}}$, thus giving a better basis of comparison. In most cases the published figures for initial pressures refer to room temperatures. Where this has been found to be otherwise, the initial pressures have been adjusted to correspond to a temperature of 15° C., and a corresponding correction applied to the maximum pressures.

Few direct determinations of explosion temperatures have been possible owing to the very high temperatures developed.

In comparing explosion times, consideration must be given to the dimensions of the explosion vessels concerned—on which they are mainly dependent.

In the following tables all results may be considered to refer to explosions of gaseous mixtures at atmospheric pressure and temperature unless specially stated otherwise.

ABBREVIATIONS

$P_{\text{max.}}/P_{\text{init.}}$	Ratio of maximum pressure developed to initial pressure.
$P_{\text{init.}}$	Initial pressure in atmospheres.
$T_{\text{init.}}$	Initial temperature in °C.
V_x	Vessel whose capacity is x cm.^{3}, unless otherwise stated.
Cyl.	Cylindrical.
Con.	Conical.
Sphere	Spherical.
Milli-sec.	Time in milli-seconds to attain maximum pressure.

H_2 HYDROGEN

Mixture.	$\frac{P_{\text{max.}}}{P_{\text{init.}}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$2H_2$				
$+O_2$	9·5		Cyl., V_{18}	(2)
$+O_2+4N_2$	6·5	10	Cyl., V*	(6)
$+O_2$	9·25		Cyl., V_{4000}	(9)
$+O_2+2H_2$	8·34			
$+O_2+4H_2$	7·58			
$+O_2+6H_2$	6·67			
$+O_2+2O_2$	8·2			
$+O_2+6O_2$	6·4			
$+O_2+N_2$	8·65			
$+O_2+2N_2$	8·26			
$+O_2+4N_2$	7·5			
$+O_2+6N_2$	6·5			
$+2N_2O$	12·85			
$+2N_2O+2N_2$	10·47			
$+O_2$	7·41	1·04	Cyl., V_{300}	(11, 15)
$+O_2$	9·69	2·14	Cyl., V_{4000}	(11, 15)
$+O_2+\frac{1}{20}H_2$		2·27	Cyl., V_{4000}	(11, 15)
$+O_2+\frac{1}{10}H_2$		2·53		
$+O_2+\frac{1}{5}H_2$		2·41		
$+O_2+H_2$		2·82		
$+O_2+2H_2$		1·67	Cyl., V_{300}	(11, 15)
$+O_2+2H_2$		4·22	Cyl., V_{4000}	(11, 15)
$+O_2+3H_2$		5·95		
$+O_2+4H_2$		9·67		
$+O_2+2O_2$		8·16		
$+O_2+6O_2$		16·04		
$+O_2+N_2$		2·86		
$+O_2+\frac{1}{2}N_2$		3·55		
$+O_2+2N_2$	8·63	6·87		
$+O_2+2N_2$	7·60	2·67	Cyl., V_{300}	(11, 15)
$+O_2+4N_2$	7·55	11·98	Cyl., V_{4000}	(11, 15)
$+O_2+4N_2$	7·34		Cyl., V_{300}	(11, 15)
$+O_2+6N_2$	6·64	24·45	Cyl., V_{4000}	(11, 15)
$+O_2+6N_2$	6·12		Cyl., V_{300}	(11, 15)
$+O_2+8N_2$		36·35	Cyl., V_{300}	(11, 15)
$+O_2$	8·48		Cyl., V_{4000}	(13). Cf. (5, 7)
$+O_2+2O_2$	8·37			
$+O_2+3O_2$	7·94			
$+O_2+6O_2$	7·0			
$+O_2+3H_2$	8·02			
$+O_2+4N_2$	6·8	9·5	Con., V_{115} in.^{3}, ignit. at vertex	(68)
$+O_2+4N_2$	7·54†	8·4	1·15 $P_{\text{init.}}$ atm.; Cyl., V*, $T_{\text{init.}}=54°$ C.	(75)
$+O_2+4N_2$	7·96†	6·9	310	
$+O_2+4N_2$	8·14†	6·1	5·5	

* Diam. 7 inch, depth 8 inch.

† Calcd. to $T_{\text{init.}}=15$ °C.

H_2 HYDROGEN—*Continued*

Mixture.	$\frac{P_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$2H_2$				
$+O_2+4N_2$	7·98	5·5	$T_{init.}$ = 15° C. $P_{init.}$ = 2 atm. Cyl., *V**	(75)
$+O_2+2N_2$	8·28	2·2		
$+O_2+4H_2$	8·1	1·0		
$+O_2+2H_2$	9·13	1·0		
$+O_2$	9·3	0·7		
$+O_2+4O_2$	7·7	2·9		
$+O_2+2O_2$	8·8	1·5		
$+O_2+4CO_2$	5·65	25·5		
$+O_2+2CO_2$	7·10	4·6		
$+O^2+4N_2$	7·7	5 or less, decreasing at higher $P_{init.}$	3 $P_{init.}$; Sphere V_{240} $T_{init.}$ = 17° C.	(79)
	7·8		10	
	8·0		25	
	8·1		50	
	8·33		75	
	8·50		100	
	8·64		125	
	8·67		150	
	8·80		175	
$+O_2+4N_2$	7·7		Same as above except $P_{max.}/P_{init.}$ has been corrected. $P_{max.}$ for cooling losses during combustion period ; $P_{init.}$ for deviation from Boyle's law.	(79)
	7·84			
	8·05			
	8·16			
	8·43			
	8·63			
	8·79			
	8·82			
	8·98			
H_2				
$+N_2O$		2·06	Cyl., V_{300}	(11, 15)
$+Cl_2+3{\cdot}6H_2$	6·88		Cyl., V_{4000}	(13). Cf (5, 7)
% H_2 in air	Values calculated from published temp. estimates.			
25·4	7·23		Cyl., *V* 30 cm. diam., 30 cm. deep.	(61)
15·3	5·03			
10·0	4·03			

* Diam. 7 inch, depth 8 inch.

CO CARBONIC OXIDE

Mixture.	$\frac{P_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$2CO$				
$+O_2$	10·1		Cyl., V_{18}	(2)
$+O_2+4N_2$	7·3		Cyl., V_{18}	(2)
$+O_2$	9·56		Cyl., V_{4000}	(9)
$+O_2+N_2$	8·82			
$+O_2+2N_2$	8·28			
$+O_2+5N_2$	6·66			
$+O_2$	9·42		Cyl., V_{4000}	(13). Cf. (5, 7)
$+O_2+1\frac{1}{2}CO_2$	7·50			
$+O_2+3CO_2$	6·50			
$+O_2+4\frac{1}{2}CO_2$	4·8			
$+O_2+1\frac{1}{2}CO$	8·33			
$+O_2+6CO$	7·01			
$+O_2+1\frac{1}{2}O_2$	8·52			
$+O_2+6O_2$	6·40			
$+O_2+3\frac{3}{4}N_2$	7·24			
$+O_2+7\frac{1}{2}N_2$	5·98			
$+O_2$	9·29	12·86	Cyl., V_{300}	(11, 15)
$+O_2$	9·93	15·51	Cyl., V_{4000}	(11, 15)
$+O_2+N_2$		17·78	Cyl., V_{300}	(11, 15)
$+O_2+2N_2$		26·49	Cyl., V_{300}	(11, 15)
$+O_2+CO_2$		27·18	Cyl., V_{300}	(11, 15)
$+O_2+2CO_2$		35·80	Cyl., V_{300}	(11, 15)
$+O_2$	10·0	12·5	4·3 Sphere	(73)
$+O_2$	11·5	5·0	21·4 $P_{init.}$ V_{240}	
$+O_2$	12·1	5·0	50·0 $T_{init.} = 17°$ C.	
$+O_2+2A$	10·6	10	Sphere, V_{240} $P_{init.} = 35·7$ $T_{init.} = 17°$ C.	(69)
$+O_2+2O_2$	10·3	5		
$+O_2+2CO$	10·01	5		
$+O_2+2N_2$	9·55	40		
$+O_2+4A$	10·20	25	Sphere, V_{240} $P_{init.} = 50$ $T_{init.} = 17°$ C.	(69)
$+O_2+4O_2$	9·20	5		
$+O_2+4CO$	9·00	10		
$+O_2+4N_2$	8·30	190		
$+O_2+6A$	9·7	140	Sphere, V_{240} $P_{init.} = 64·3$ $T_{init.} = 17°$ C.	(69)
$+O_2+6CO$	7·9	130		
$+O_2+6N_2$	6·4	1100		
$+O_2+4A$	8·5	35	3·0	(79)
	8·9	50	10·0	
	10·2	25	50·0 Sphere	
	10·53	15	75·0 $P_{init.} V_{240}$	
	10·63	10	100·0 $T_{init.} = 17°$ C.	
	11·2	10	125·0	
	11·66	10	150·0	
$+O_2+4A$	8·65	Same as above except $P_{max.}/P_{init.}$ has been corrected; $P_{max.}$ for cooling loss during combustion period; $P_{init.}$ for deviation from Boyle's law.		(79)
	9·1			
	10·1			
	10·3			
	10·33			
	10·84			
	11·4			

CARBONIC OXIDE—*Continued.*

Mixture.	$\frac{P_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$+O_2+4O_2$	7·6	60	3·0 Sphere $P_{init.}$ V_{240} $T_{init.}=17°$ C.	(73)
	7·7	45	10·0	
	8·6	10	25·0	
	9·2	5	50·0	
	10·1	5	75·0	
$+O_2+4CO$	9·6	10	75·0 Sphere $P_{init.}$, V_{240} $T_{init.}=17°$ C.	(79)
	9·8	5	100·0	
	10·0	5	125·0	
	10·13	5	150·0	
$+O_2+4CO$	9·48	Same as above except $P_{max.}/P_{init.}$ corrected for combustion period loss and deviation from Boyle's law.		(79)
	9·68			
	9·95			
	10·16			
$+O_2+4N_2$	7·13	70	3·0 Sphere, V_{240} $P_{init.}$. $T_{init.}=17°$ C.	(79)
	7·5	100	10·0	
	7·72	150	25·0	
	8·20	190	50·0	
	8·47	320	75·0	
	8·80	400	100·0	
	8·88	470	125·0	
	9·03	530	150·0	
	9·23	560	175	
$+O_2+4N_2$	7·80	Same as above except $P_{max.}/P_{init.}$ corrected for combustion loss and deviation from Boyle's law.		(79)
	8·00			
	8·30			
	8·65			
	9·14			
	9·37			
	9·45			
	9·76			
	10·17			
CO				
$+N_2O$	10·78		Cyl., V_{40}	(9)
$+N_2O$		15·40	V_{300}	(11, 15)

Influence of the amount of water vapour present. 29·3 % CO in air.

Vol. of H_2O of Vapour added to 100 of Mixture.	$\frac{P_{max}}{P_{init}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
0	7·72*	290·2	Cyl. V, 7 in. diam., 8 in. deep. $T_{init.}=50°$ C. $P_{init.}=5$.	(83)
2·56	7·93*	90·1		
1·68	7·94*	97·0		
1·67	7·94*	92·0		
1·24	7·96*	101·5		
1·21	7·96*	101·0		
0·60	7·94*	125·9		
0·30	7·89*	166·3		

* Calcd. to $T_{init.}=15°$.

MIXTURES OF H_2 AND CO

Mixture.		$\frac{P_{max.}}{P_{init}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
2CO					
$+H_2+1\frac{1}{2}O_2$		9·28		Cyl., V_{4000}	(9, 15)
$+H_2+4O_2$		8·3			
$+3H_2+1\frac{1}{2}O_2$		8·92			
$+4H_2+3O_2$		9·08			
$2H_2+O_2$			1·04	Cyl., V_{300}	(11)
$2CO+O_2$			12·86	Cyl., V_{300}	(11)
$2H_2$					
$+CO+1\frac{1}{2}O_2$			2·57	Cyl., V_{300}	(11)
$+CO+O_2$			1·39	Cyl., V_{300}	(11)
H_2					
$+CO+O_2$			3·88	Cyl., V_{300}	(11)
$+2CO+1\frac{1}{2}O_2$			4·14	Cyl., V_{300}	(11)
$2(xH_2+yCO)+O_2+4N_2$					
x.	y.				
100	0	8·10*	7·5	Cyl. V, 7 in. diam., 8 in. deep. $P_{init.}=5$. $T_{init.}=50°$ C.	(83)
49·7	50·3	8·10*	15·5		
24·8	75·2	8·10*	29·3		
11·9	88·1	8·10*	46·5		
8·0	92·0	8·10*	56·6		
4·1	95·9	8·05*	75·9		
0·2	99·8	7·79*	245·9		
$2(xH_2+yCO)+O_2+4N_2$.					
100	0	7·82	5	Sphere, V_{240} $T_{init.}=17°$ C. $P_{init.}=50$.	(67)
50	50	7·98	15		
25	75	8·2	15		
12·5	87·5	8·2	25		
8	92	8·5	25–30		
4	96	8·5	30		
0	100	8·4	180		

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* Calcd. to $T_{init.}=15°$.

CH_4 METHANE

Mixture.	$\frac{P_{max}}{P_{init}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
CH_4				
$+1{\cdot}84O_2$ - -	14·35		Cyl., V_{4000}	(13)
$+2{\cdot}8O_2+10{\cdot}5N_2$	7·9			
$+1{\cdot}92O_2+7{\cdot}24N_2$	8·95			
$+1{\cdot}44O_2+5{\cdot}41N_2$	7·98			
$+2O_2$ - -	15·44		Cyl., V_{4000}	(9, 15)
$+2O_2$ - -	13·94	1·24	Cyl., V_{300}	(11, 14)
$+O_2+4N_2$ -	5·6	80	Sphere, V_{240} $P_{init.} = 50$ $T_{init.} = 17°$ C.	(53)
% CH_4 in air				
6·30	4·20		Sphere, V_{4000}; polished interior surface	(54)
6·80	6·10			
7·45	6·64			
7·95	7·09			
8·45	7·40			
9·20	7·73			
9·40	7·80			
9·65	7·90			
10·10	7·97			
10·25	7·97			
10·75	7·87			
11·40	7·73			
12·10	7·36			
12·90	6·78			
13·40	5·80			
13·90	4·50			
6·05	3·86		Sphere, V_{16000}; polished interior surface	(54)
6·85	5·35			
7·80	6·85			
8·80	7·66			
9·80	7·94			
10·80	7·80			
11·90	7·40			
12·80	6·78			
12·1	8·15*	275·9	$T_{init.} = 100°$ C. Cyl. V, 7 in. diam., 8 in. deep. $P_{init.} = 6{\cdot}5$.	(83)
11·0	8·56*	140·6		
10·5	8·69*	119·3		
9·9	8·70*	105·8		
9·7	8·77*	106·5		
8·5	8·19*	128·8		
7·3	7·20*	225·9		

* Calcd. to $T_{init.} = 15°$.

C_2H_2 ACETYLENE

Mixture.	$\frac{P_{max.}}{P_{init}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$C_2H_2+2\frac{1}{2}O_2$ -	14·45		Cyl., V_{4000}	(9, 15)
$C_2H_2+2\frac{1}{2}O_2$ -		1·94	Cyl., V_{300}	(11)

C_2H_4 ETHYLENE

Mixture.	$\frac{P_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$C_2H_4+3O_2$ -	15·25		Cyl., V_{4000}	(9, 15)
$C_2H_4+3O_2$ -	14·18	2·86	Cyl., V_{300}	(11, 14)
$C_2H_4+3O_2$ -	15·73	2·23	Cyl., V_{4000}	(11, 14)

C_2H_6 ETHANE

Mixture.	$\frac{P_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$C_2H_6+3\frac{1}{2}O_2$ -	15·30		Cyl., V_{4000}	(9)
$C_2H_6+3\frac{1}{2}O_2$ -		0·83	Cyl., V_{300}	(11)
% C_2H_6 in air				
3·05	3·8		Deduced from a published curve.	(56)
3·3	4·9			
3·6	5·75			
4·05	6·85			
4·8	7·8			
5·6	8·3			
6·7	8·75			

C_2H_6O METHYL ETHER

Mixture.	$\frac{P_{max.}}{P_{init}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$C_2H_6O+3O_2$ -	18·82		Cyl., V_{4000}	(9)

$C_4H_{10}O$ ETHYL ETHER

Mixture.	$\frac{P_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
$C_4H_{10}O+6O_2$ -	15·42		Cyl., V_{4000}	(9)

C_2N_2 CYANOGEN

Mixture.	$P_{max.}/P_{init.}$	Milli-sec.	Experimental Conditions.	Literature Ref.
C_2N_2				
$+O_2+4N_2$	10·95		Cyl., V_{18}	(2)
$+2O_2$	19·80		Cyl., V_{4000}	(9, 15) Cf. (5, 13)
$+N_2+2O_2$	16·72			
$+2N_2+2O_2$	13·93			
$+4N_2+2O_2$	11·66			
$+O_2$	23·72			
$+\frac{3}{4}N_2+O_2$	19·52			
$+2N_2+O_2$	14·42			
$+4N_2+O_2$	11·14			
$+4NO$	16·00			
$+N_2O$	21·40			
$+2NO$	22·08			
$+2N_2O$	24·6			
$+O_2$		1·06	Cyl., V_{300}	(11)
$+2O_2$		1·55	Cyl., V_{300}	(11)
$+2O_2$		4·50	Sphere, V_{1500}	(11)
$+2O_2+2N_2$		15·4	Cyl., V_{300}	(11)
$+2O_2+N_2$		6·09	Cyl., V_{300}	(11)
$+O_2+\frac{3}{4}N_2$	18·65	3·20	Cyl., V_{300}	(11)
$+O_2+\frac{3}{4}N_2$	21·09	2·74	Sphere, V_{1500}	(11)
$+O_2+3N_2$	13·88	10·35	Cyl., V_{300}	(11)
$+O_2+3N_2$	15·56	15·12	Sphere, V_{1500}	(11)
$+O_2+3N_2$		23·63	Cyl., V_{300}	(11)
$+O_2+4N_2$	10·6	29·78	Cyl., V_{300}	(11)
$+4N_2O$		4·53	Cyl., V_{300}	(11)
$+4N_2O$	12·02		Sphere, V_{1500}	(11)

C_6H_6 BENZENE

Mixture	$P_{max.}/P_{init.}$	Milli-sec.	Experimental Conditions.	Literature Ref.
Ratio Air/Benzene by weight.				(82)
16·84	8·28*	105·1	$T_{init.}=100°$ C. $P_{init.}=95$ lbs. (sq. in.). Cyl. $V.$, 7 in. dia., 8 in. deep.	
14·76	9·00*	73·5		
13·24	9·50*	59·7		
13·16	9·50*	59·8		
12·06	9·74*	55·1		
10·7	9·78*	49·0		
9·15	†	†		

* Calcd. to $T_{init.}=15°$ C.

† Loud metallic knock.

C_6H_{14} HEXANE

Mixture.	$\frac{P'_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
Ratio Air/Hexane by Weight.				(82)
16·91	8·86*	91·2	$T_{init.}$ = 100° C. $P_{init.}$ = 95 lbs./sq. in. Cyl. V., 7 in. dia., 8 in. deep.	
14·80	9·48*	69·5		
13·97	9·56*	64·0		
13·20	9·50*	58·6		
10·72	†	†		

PETROL

Mixture.	$\frac{P_{max.}}{P_{init.}}$	Milli-sec.	Experimental Conditions.	Literature Ref.
Ratio Air/Petrol by Weight.				(82)
19·2	7·74*	175·2	$T_{init.}$ = 100° C. $P_{init.}$ = 95 lbs./sq. in. Cyl. V., 7 in. dia., 8 in. deep.	
16·9	8·58*	109·6		
14·8	9·33*	78·4		
13·0	9·71*	67·1		
10·7	‡	‡		

* Calculated to $T_{init.}$ = 15° C. † Violent explosion. ‡ Loud metallic knock.

INFLUENCE OF INITIAL TEMPERATURE AND PRESSURE ON BENZENE-AIR EXPLOSIONS (82)

Initial Pressure. lbs./sq.in.	Initial Temperature.	Maximum Pressure Rise, lbs./sq. in.		
		12 to 1 Mixture by Weight.	10·7 to 1 Mixture by Weight.	9·15 to 1 Mixture by Weight.
95·0	100° C.	645	644	—
67·0		447	449	—
38·0		242	248	241
120·5	200° C.	636	—	646
84·5		438	—	442
48·2		238	—	240
146	300° C.	614	—	633
102		420	—	434
58		226	—	237

COMPARISON WITH PETROL AND HEXANE

Initial Pressure. lbs./sq. in.	Initial Temperature.	Air/Petrol by Weight.	Air/Hexane by Weight.	Air/Benzene by Weight.
		13	14	12
100	100° C.	660	668	680
50		321	324	327
100	200° C.	519	529	523
50		250	250	248

INFLUENCE OF TEMPERATURE AND PRESSURE ON METHANE-AIR AND HYDROGEN-AIR EXPLOSIONS (83)

(See Text, pp. 270—271.)

THERMAL EQUILIBRIUM IN COAL-GAS-AIR EXPLOSIONS (31)

(See Text, pp. 240—242.)

DIRECT MEASUREMENT OF THE TEMPERATURE-CYCLE IN A GAS ENGINE (47); Cf. (18, 20, 38)

Coal-gas (460 B.Th.U./ft^3.); cylinder 7 in. diameter; stroke 15 in.; working volume 577 in.^{3}; thermocouple: 10 % alloys of Pt-Rh and Pt-Ir (0·0005–0·0008 in. thick).

No. - - - -	1	2	3	4	5
Ratio Air/Gas -	7·35/1	7·08/1	7·13/1	6·71/1	5·66/1
Jacket outlet, °C.	35·6	37·2	81·4	40·6	52·8
Angle of Crank.	Temp., °C.	Temp., °C.	Temp., °C.	Temp., °C.	Temp., °C.
360	569	568	582	705	636
300	496	503	515	624	540
240	349	348	371	517	431
180	256	269	317	422	371
120	217	223	262	365	330
60	228	241	273	326	337
30	267	275	330	339	442
720					2249
710				1947	
709					
708				1889	
705		1848	1871		1918
697	1836				
690	1546	1551	1532	1579	1721
675	1423	1418	1397	1437	1586
660	1154	1147	1269	1247	1417
645	1159	1124	1139	1193	1275
630	1041	1052	1018	1098	1192
615	1022	1007	1017	1058	1124
600	1017	975	975	982	1068
540	856	843	816	895	889
480	726	708	704	794	764
420	648	646	637	751	705

For diagram illustrating the above, see Text, page 239.

For Radiation and Conduction Losses, see Text, pages 245—254. (44, 45, 61, 64).

Various Formulae for Approximate Estimation of Cooling Losses in Explosions of Coal Gas-Air Mixtures (David).

General formula for radiation loss in coal gas-air explosions (59)

$$R_T = 0{\cdot}0001\,(T_{\text{max.}} - 700\sqrt{D \times L}),$$

where R_T = Total radiation registered,

$T_{\text{max.}}$ = Maximum temperature (mean, °Abs.),

D = Density of the gaseous mixture in atmospheres,

L = Length of the explosion cylinder in cm.,

Rate of loss of heat by radiation, cm.^{2} of wall surface. sec (R_L) (64)

$$R_L = 1{\cdot}75 \times 10^{-14}\theta^4$$

where θ = mean absolute temperature.

For a cylindrical vessel (h cm. diam. × h cm. deep)

$$R_L = 0{\cdot}32 \times 10^{-14}\theta^4\sqrt{h}.$$

Rate of loss of heat by conduction, cm.^{2} of wall surface, sec (R_c) (64)

$$R_c = 4 \times 10^{-13}(t - t_w)^4$$

for temperatures above 2000° Abs.,

$$R_c = 7 \times 10^{-10}(t - t_w)^3$$

for temperatures below 2000° Abs., where $(t - t_w)$ is the temperature difference, °C., between the hot gases and the walls of the explosion vessel.

Rate of total heat loss, cm.^{2} of wall surface, sec (H_T) in a cylinder (h cm. diam. × h cm. deep) (64).

$$H_T = 4 \times 10^{-13}\,(T - T_w)^4 + 0{\cdot}32 \times 10^{-14}\,T^4\sqrt{h}$$

for temperatures above 2000° Abs.

$$H_T = 7 \times 10^{-10}\,(T - T_w)^3 + 0{\cdot}32 \times 10^{-14}T^4\sqrt{h}$$

for temperatures below 2000° Abs.

Total heat loss to walls of cylindrical explosion vessel (30 cm. × 30 cm.) up to moment of maximum pressure (64) (coal gas-air explosions)—atmospheric density

$$H_{\text{max.}} = 2{\cdot}15 \times 10^{-8}\theta^{2\cdot5}_{\text{max.}} \times t_e$$

or expressed as a proportion of the heat of combustion

$$H_{c\ \text{max.}} = 1{\cdot}43 \times 10^{-5}\theta^{1\cdot5}_{\text{max.}} \times t_e,$$

where t_e explosion time.

Total heat loss per unit area in similar engines working under similar conditions may be given by the equation (74)

$$H = C + R\sqrt{d},$$

where C = conduction loss per unit area,

$R\sqrt{d}$ = radiation loss per unit area in an engine of diameter d.

INFLUENCE OF TURBULENCE

Cf. (68 7 31, 39, 56, 75). See Text pages, 243 and 247.

Ethane, C_2H_6, and air mixtures in spherical vessel, capacity 4000 cm.^{3} (sparked at centre) (56).

% C_2H_6 in Air.	Milli-sec.	
	With Turbulence.	Quiescent.
3·30	176	
3·45	96	
3·60		332
3·80		152
3·85	45	146
4·05	36	124
4·30	33	
4·35		94
4·60	26	
4·65		73
4·70	29	
4·80		70
5·00	24	63
5·25	21	
5·35	20	54
5·60		52
5·95	19	
6·00		46·5
6·40	19	
6·45		56
6·75	19	46·5
7·05	20	50
7·15		52

Distribution of Energy at the moment of maximum pressure (64). See Text, page 255.

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(For a key to the periodicals see pp. 534-535).

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